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The Characterization of the Chesapeake Bay
A Systematic Analysis of Toxic Trace Elements

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Sep 82

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THE CHARACTERIZATION OF THE CHESAPEAKE BAY: A SYSTEMATIC ANALYSIS OF TOXIC TRACE ELEMENTS

Howard M. Kingston, Robert R. Greenberg,
Ellyn S. Beary, Billy R. Hardas,
John R. Moody, Theodore C. Rains
Center for Analytical Chemistry

and

Walter S. Liggett
Center for Applied Mathematics

National Bureau of Standards
Washington, DC 20234

Grant No. EPA-79-D-X-0717

Project Officers

Ernest L. Garner and Howard M. Kingston
Center for Analytical Chemistry
National Bureau of Standards
Washington, DC 20234

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As part of a multidisciplinary study of the Chesapeake Bay, the National Bureau of Standards (NBS) was asked to develop the techniques and procedures necessary to measure the trace and toxic element concentrations within the water column throughout the length of the Chesapeake Bay. The Inorganic Analytical Research Division of the Center for Analytical Chemistry at NBS has completed the analysis for selected elements (Cd, Ce, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sc, Sn, Th, U, and Zn), including some elements at concentrations consistently below one picogram per milliliter (part per trillion). The characterization of the Chesapeake Bay can be divided into five major phases. The first included the development and construction of a sampling system for the trace metallic elements dissolved in water, and a filtration system for collecting the particulate elemental component.

The second phase consisted of sampling, chemical stabilization by acidification and storage of the samples in the field.

The third phase of activity consisted of the chemical separation and preparation of samples for the analytical instrumental methods. These chemical separations had been developed prior to this application.

The fourth major phase consisted of the instrumental analysis of the samples for the trace elements.

The fifth major phase involved data reduction and evaluation of the statistical significance of the blank.

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FOREWORD

This status report is submitted in partial fulfillment of the requirement and conditions of Grant Number EPA-79-D-X-0717, "The Characterization of the Chesapeake Bay: A Systematic Analysis of Toxic Trace Elements". The period covered by this report extends from April 1979 to the end of September 1981.

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BRIEF

As part of a multidisciplinary study of the Chesapeake Bay, the National Bureau of Standards (NBS) was asked to develop the techniques and procedures necessary to measure the trace and toxic element concentrations within the water column throughout the length of the Chesapeake Bay. The Inorganic Analytical Research Division of the Center for Analytical Chemistry at NBS has completed the analysis for selected elements (Cd, Ce, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sc, Sn, Th, U, and Zn), including some elements at concentrations consistently below one picogram per milliliter (part per trillion). The characterization of the Chesapeake Bay can be divided into five major phases. The first included the development and construction of a sampling system for the trace metallic elements dissolved in water, and a filtration system for collecting the particulate elemental component. This sample collection system consisted of an all plastic system, using a magnetically driven plastic pump with conventional polyethylene tubing, and included conventional polyethylene storage drums of high purity water used in flushing of the system. The apparatus was designed and constructed at NBS.

The second phase consisted of sampling, chemical stabilization by acidification and storage of the samples in the field. This was accomplished aboard the R/V Retriever, with the cooperation of both the Maryland Geological Survey and Virginia Institute of Marine Sciences, for sample logistics and acquisition. The total complement of 102 samples was obtained, filtered, acidified and stabilized. There were also 51 replicate bottom samples obtained and frozen for archival use. A series of over 30 blanks were also prepared and integrated with the 102 water samples to be analyzed. The stabilization and storage of the water samples used some of the methodology and experience gained on SRM 1643a, Trace Elements in Water, and stability studies of a quantity of Chesapeake Bay water which has been under study for several years.

The third major phase of activity consisted of the chemical separation and preparation of samples for the analytical instrumental methods. These chemical separations had been developed prior to this application. A few post separation matrix alterations were made for specific instrumental efficiency optima. The chemical manipulation involved the preparation of samples for analysis using two major instrumental efforts, neutron activation analysis (NAA) and graphite furnace atomic absorption (GFAA). A major portion of this effort also involved quality assurance. This was partially accomplished by utilizing standards preparation and NBS Standard Reference Materials (SRM's), specifically Trace Elements in Water, 1643a; interspersion of these materials was utilized in the chemical and instrumental phases of the work. The chemical separation/sample preparation stage of this work has been described in the literature for both instrumental techniques [1,2].

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The fourth major phase consisted of the instrumental analysis of the samples for the trace elements. This phase places most of the burden for analysis on NAA and GFAA with isotope dilution mass spectrometry (IDMS) contributing isotopic and concentration data for uranium. The total number of elemental concentrations resulting from the analyses of the contracted elements exceeded 3,000 and involved several thousand more unreported analyses totaling over 5,000 separate determinations.

The fifth major phase involved data reduction and evaluation of the statistical significance of the blank. The blanks were statistically modeled for each element, and the blank and uncertainty of the blanks were applied to the data. The concentrations were adjusted uniformly to at least the 95% confidence limit.

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INTRODUCTION AND HISTORY

This report describes the National Bureau of Standards (NBS) efforts in a multidisciplinary study of the Chesapeake Bay coordinated by the Chesapeake Bay Program Office of the U. S. Environmental Protection Agency. The NBS used the best available technology to determine the trace and toxic element concentrations in the water column. As part of this program, the NBS has collected and analyzed both the dissolved and suspended particulate fractions of 102 water samples covering the entire length of the Chesapeake Bay. The elements of interest include Cd, Ce, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sc, Sn, Th, U, and Zn. These analyses were accomplished using specific chemical preconcentration, separations and manipulations to prepare the samples for analysis by Neutron Activation Analysis (NAA) and Graphite Furnace Atomic Absorption Spectrometry (GFAAS).

The literature of marine water analysis reflects the considerable difficulty in establishing an accurate and precise method of analysis for trace metals. A seawater matrix defies a simplified approach. For example, specific sampling techniques, container contamination, suspended particulate matter, and analytical techniques have to be considered. The solving of the analytical problem is of little value unless a representative sample can be obtained free of contamination and properly stored until analysis.

In recent years, methods have been developed to determine trace elements in seawater by X-ray fluorescence [4], neutron activation [5,6], spectrophotometry [7], anodic stripping voltammetry [8], and atomic absorption spectrometry [9-11]. However, each of these analytical techniques requires a preliminary separation. Fabricand, et al. [12], reported the direct determination of Cu, Fe, Mn, Ni, and Zn in seawater by atomic absorption spectrometry (AAS) using an air-acetylene flame, but other workers have reported difficulties using their technique because of light scattering and burner clogging.

Except for neutron activation analysis and anodic stripping voltammetry, no analytical techniques are currently available for the untreated sample determination of trace elements in seawater at concentrations below $5\ \mu g\ L^{-1}$. Usually it is necessary to preconcentrate the trace elements from a large volume and separate the transition elements from the alkali and alkaline earth elements. In such sample preparations, the efficiency of concentration, completeness of separation, and total analytical blank become critical to the final instrumental method [13].

Preconcentration techniques which have been used include coprecipitation [14], chelation and extraction [15], and chelating ion-exchange resin [13,16].

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Most of these separation and concentration methods require large volumes of chemicals which can lead to high blanks unless the reagents have been carefully purified.

Of the presently used preconcentration techniques, Chelex 100 chelating resin has been shown to be efficient and yields low analytical blanks [17]. Applications of Chelex 100 resin for trace metal preconcentration from seawater have been reviewed by Riley and Skirrow [13]. Chelex 100 is a strong chelator and removes metal ions from most known naturally occurring chelators in seawater [17-19]. The resin will not, however, remove metals held in organic and inorganic colloids which can be present even after ultrafiltration. Precautions must be taken to destroy such colloids prior to collection of the ions by the resin. Florence and Batley have reported destroying interfering organic colloids by the addition of 0.16 M nitric acid and heat and also by using ultraviolet irradiation of the sample prior to collection on the resin [18,19]. While excellent recovery and low analytical blanks are achieved, relatively high concentration of Na, K, Ca, and Mg are retained with the trace metals. The concentrations of these interfering alkali and alkaline earth salts in the final sample are in milligram quantities, as compared to the microgram and submicrogram quantities of concentrated trace metals. The alkali and alkaline earth ions occupy the resin sites not occupied by the transition metals and are co-eluted with the metals when using acids [16].

A more recent separation procedure utilizing Chelex resin produced a sample devoid of alkali, alkaline earth, and halogen elements, and left a dilute nitric acid/ammonium nitrate matrix containing only the trace elements of the seawater sample (Kingston and Rains, et al. [1]). This procedure was used in conjunction with GFAA to analyze Chesapeake Bay estuarine and Gulf of Alaska seawater samples [1]. The method was also modified and the resin was irradiated directly without elution, in conjunction with a NAA technique utilizing these same samples and NBS SRM 1643a, a trace element water standard [2]. The technique has also been applied to x-ray fluorescence (XRF), utilizing the same Chesapeake Bay water sample and NBS SRM's 1648 and 1632, environmental samples, urban particulate and trace elements in coal [3].

With the graphite furnace it is possible to determine 10^{-9} to 10^{-12} g of many of the trace elements in seawater. However, the high salt content (35 g/kg) in marine water makes it difficult to effectively volatilize the matrix without loss of analyte. The major component in seawater is sodium chloride which has a relatively high volatilization temperature. Also, the trace metals in seawater are present as chlorides, which have a lower volatilization temperature. Therefore, it is difficult to volatilize the sodium chloride during the ashing step without losses of the analyte. Calcium and magnesium chloride are also present in seawater in large quantities, and a temperature greater than 2000 °C is required to volatilize these elements. Thus, even if the sodium chloride were removed during the ashing step using matrix modification [20], residual calcium and magnesium chlorides remain to interfere with the analyte during atomization. These factors make separation prior to GFAA analysis necessary.

While the Chelex resin procedure produces a highly desirable and appropriate aqueous matrix for most spectroscopic methods of analysis, a solid sample would be more appropriate for other instrumental techniques [3] such as XRF or NAA [2]. In addition, the above separation procedure also makes it difficult or impossible to analyze several elements which are held strongly by the resin but cannot be quantitatively eluted. Chromium and vanadium exhibit this type of behavior, and attempts to reproducibly elute these elements from Chelex 100 have not been totally successful.

NAA has the inherent sensitivity and accuracy to determine a number of important trace elements in seawater at their naturally occurring levels. Unfortunately, a salt water matrix is not well suited for activation analysis. The use of liquid samples limits both the amount of material and the length of irradiation available in most reactor facilities. The high levels of Na, Cl, and Br produce an extremely high background level of radiation that totally obscures the signals of most elements whose neutron activation products have comparable half-lives.

Greenberg and Kingston [2] described a method of preparation for solid samples from 100 mL of estuarine or seawater, using Chelex 100 resin, followed by the determination of 12 trace elements by NAA. Using this procedure, typical reduction factors of $\geq 10^7$ for Na, $\geq 10^5$ for Cl, and $\geq 10^3$ for Br are observed. This procedure has been used to analyze NBS SRM 1643a, as well as high salinity water samples collected near the mouth of the Chesapeake Bay.

Although one of the major advantages usually associated with NAA is the possibility of post-irradiation chemistry thus eliminating the problems associated with reagent blank and other types of contamination, the use of pre-irradiation chemistry for high-salinity waters has significant advantages. The removal of Na, Cl, and Br greatly reduces the background level of radiation during short and intermediate counts, and allows the determination of elements not otherwise possible without some type of separation. The removal of the matrix elements also greatly reduces the radiation dose received by personnel, especially if radiochemistry is used. The preconcentration of 100 100 mL of liquid to a sample of less than 0.5 gram increases the sensitivities for most elements and allows more samples to be irradiated within a single rabbit. Although other non-chemical concentration steps, such as lyophilization, could be employed prior to irradiation; they are relatively difficult to use with high salinity water, they leave the salts with the elements of interest, and can also increase the blank from the equipment used. Finally, the use of Chelex 100 prior to irradiation produces a solid sample which eliminates the problems of storage, irradiation, and handling liquid samples for NAA.

Even without pre-chemistry, the number of sample manipulation steps required before the irradiation of a high salinity water sample is considerable, including: collection; filtration; stabilization (usually by acidification); storage and encapsulation for irradiation. Extreme care during all these steps is necessary to prevent contamination of the samples. Extending the pre-irradiation treatment to include the Chelex 100 concentration/separation step produces significant benefits for the additional effort required.

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EXPERIMENTAL

REAGENTS

High purity water, nitric and glacial acetic acids were prepared using subboiling distillation at NBS [21]. All reagents used in the separation process were prepared in this manner and stored in clean FEP Teflon bottles unless otherwise stated.

Ammonium hydroxide solution was prepared by bubbling filtered ammonia gas through high purity water until room temperature saturation was achieved.

A 1.0 M ammonium acetate solution was prepared by mixing 60 g of purified glacial acetic acid and 62 g of saturated NH_4OH and diluting to 1 L in a pre-cleaned polypropylene volumetric flask. The acidity was adjusted to a pH range of 5.1 to 5.4 by dropwise addition of acetic acid and/or NH_4OH.

All reagent and sample preparations were done in a class 100 clean air laboratory [22].

Chelex 100 chelating resin, 200-400 mesh size, was purchased from Bio-Rad Laboratories.

SAMPLES

The 102 water samples were obtained from June 12, 1979, to July 6, 1979, and the sampling area extended from the mouth of the Chesapeake Bay or coastal Atlantic Ocean water to the mouth of the Susquehanna River. A map showing these approximate sample locations can be seen in Figure 1. The sampling locations, the time sampled, and the sample patterns were coordinated by Maryland Geological Survey and Virginia Institute of Marine Science. The Maryland Geological Survey station reference numbers, the date, time, depth, number of filters used, density and sample number for the samples is compiled in Appendix 1.

SAMPLING EQUIPMENT AND PLACEMENT

The sampling equipment was designed for cleanliness and the ability to take a sample with a minimum of elemental perturbation and contamination. Simplicity was also a consideration, since the field operation of the system could be under extremes in weather and physical conditions.

The system used a magnetically-driven, glass-filled, epoxy-resin pump (using ceramic bushings). The pump assembly was dismantled and subjected to

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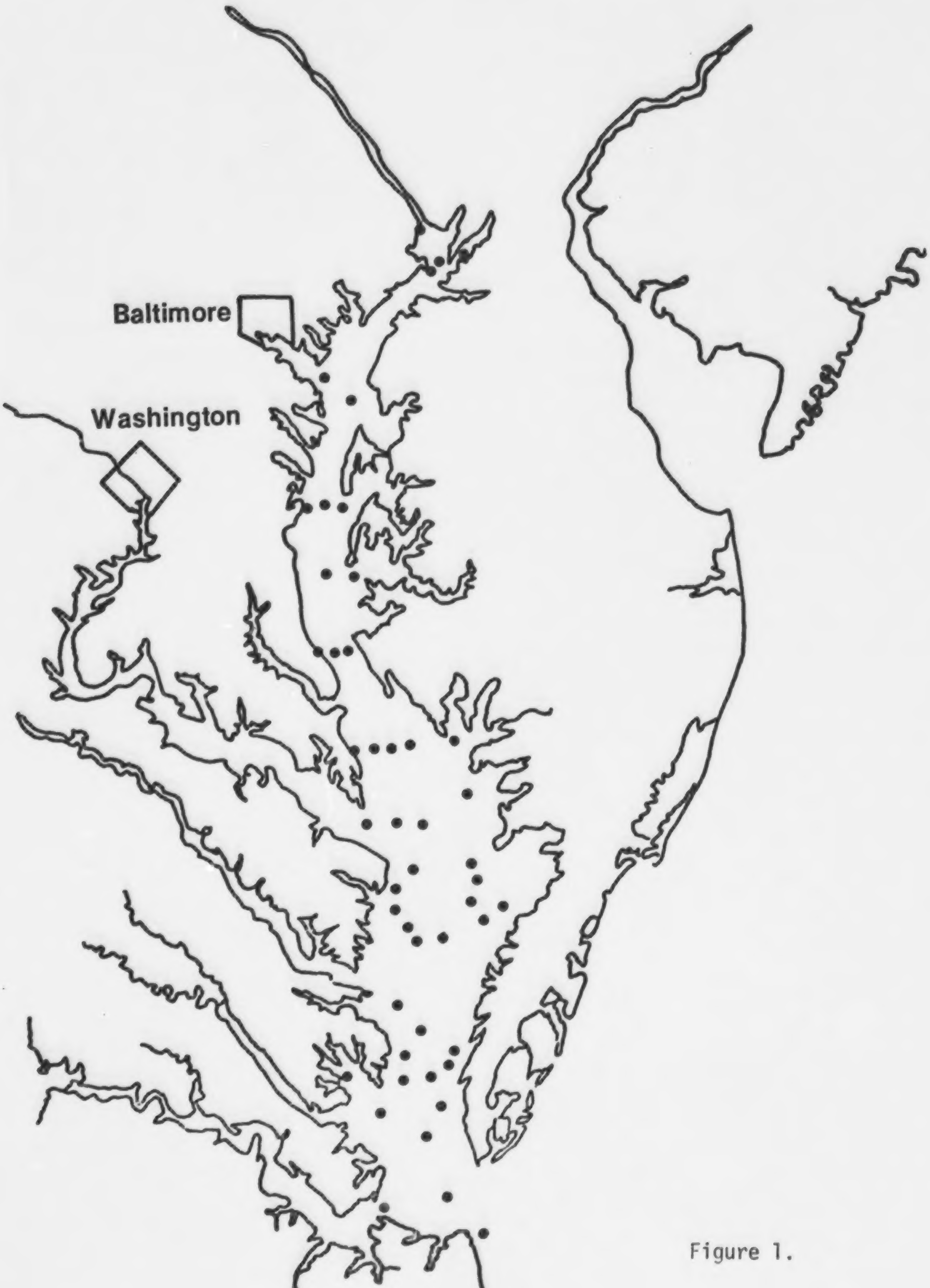
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Figure 1.

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XRF analysis and found to contain only trace quantities of one element being investigated. Only iron at the μg level was detected using the full depth of the energy dispersive x-ray system.

The tubing used was conventional polyethylene (CPE) of 1 inch (2.5 cm) in diameter. It was connected to the pump and storage by polyvinylchloride (PVC) valves, tubing connectors or T's. The lowering mechanism was a manually operated wooden drum sealed with polyurethane. The tubing was placed through a polyethylene sling on a ship's davit and extended approximately 1 meter from the ship for bottom sampling. The depth was marked on the tubing with plastic tape at 5-ft. (1.52 m) intervals. The bottom sampler consisted of a 200-ft. (61 m) coil of tubing joined using one PVC connector. The bottom of the tubing was coiled with the opening pointing up. A concrete weight inside a 1/8-inch (0.32 cm) PVC plastic was coated with paraffin and suspended 1 meter from the tubing opening using polypropylene cord. The polyethylene tubing, being less dense than water, would float if the weight actually touched bottom. However, the depth of the sampling site was monitored using the ship's depth sensing equipment, and the lowering of the equipment stopped above bottom, using the known depth and the length of the tubing lowered. The bottom sample was taken nominally 1 meter from the bottom although in a few cases this distance was greater due to current affect. The surface samples were taken in two ways, with two different techniques, depending on the current.

In minimal or no current (only 5% of the surface samples), a specially constructed float was placed on a 50-ft. (15 m) piece of 1 inch (2.5 cm) CPE tubing and held 7 m from the side of the ship, with the tubing 1 meter down pointing at a 30° angle away from the ship. The float was constructed of a 3-inch (7.6 cm) block of styrofoam, sandwiched between two sheets of plexiglass sealed using silicon sealant, with a plexiglass tube to guide the CPE sample tube and plexiglass hook. To the hook was attached a 24-ft. (7.3 m) stainless steel rod all totally encased in 1/8 inch (0.32 cm) of CPE which had been heat sealed.

The majority of surface samples (95% of the samples) was taken with the CPE tube taped 2 meters above the polyethylene encased hook previously described. The hook was inserted into the water holding 1 meter of the CPE tube below the water surface from the bow of the ship into the current.

The pumping equipment was a sealed system, and only the bottom sampler and surface sampler were exchanged using a PVC disconnect. No glue was used; the system was held together entirely by pressure-fitting tubing over PVC connectors and then clamping using stainless steel hose clamps externally. Once assembled, no pieces of equipment were replaced. A diagram of the sampling system can be seen in Figure 2.

The filtering and stabilization of the samples were accomplished in a small laboratory module on the stern of the ship, equipped with a class 100 clean bench. The work surface was covered with a plastic adhesive-backed paper used in the NBS clean laboratory for a bench covering to seal the working surface.

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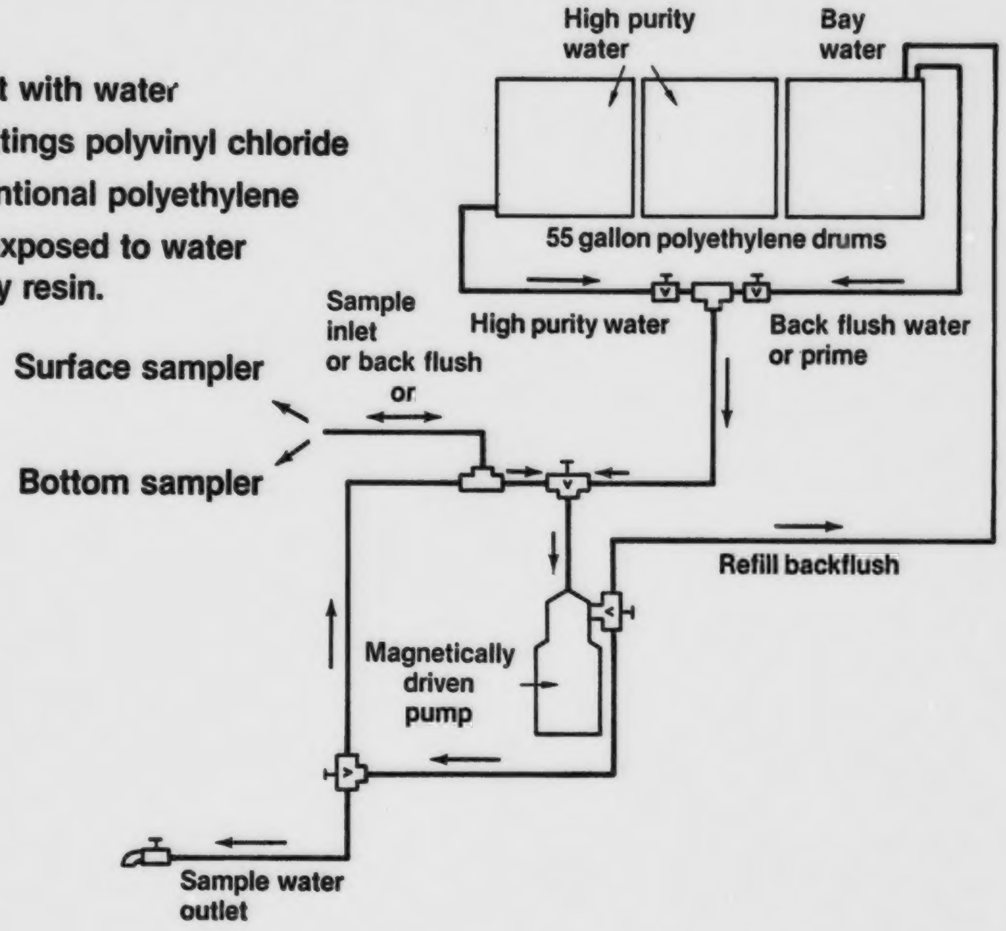
Sampler Pumping System

Materials in contact with water

1. All valves and fittings polyvinyl chloride
2. All tubing conventional polyethylene
3. All pump parts exposed to water glass filled epoxy resin.



High purity water
Bay water
55 gallon polyethylene drums
Sample inlet or back flush or
High purity water
Back flush water or prime
Surface sampler
Bottom sampler
Refill backflush
Magnetically driven pump
Sample water outlet

Figure 2.

The filtering was accomplished utilizing Amicon and Millipore 0.45 micrometer filters, each from a single lot. The filter holders were Bio-Rad Laboratories polypropylene filter holders modified with a Teflon tube on the exit. This tube fit through a hollow polyethylene stopper in a large bell jar, and the sample bottle was placed in the bell jar under the filter apparatus.

The acid was added from a quartz repipet constructed to deliver precisely 32 mL repeatedly to all sample bottles.

The sample bottles were all polyethylene CPE from a single lot of plastic. They were cleaned in 1:4 HCl and 1:4 HNO_3 acid, alternately, for two weeks in each acid, then rinsed and filled with high purity water [23]. Their variance in volume was investigated prior to use.

A discussion of the cleaning and suitability of the plastics and materials used for construction and storage in trace chemical analysis is given by Moody and Lindstrom [23].

These bottles were given a number, using the 11,000 series. Teflon FEP bottles for long-term storage were numbered in the 10,000 series. These numbers were inscribed onto the surfaces of the bottles.

SAMPLING PROCEDURE

Two primary considerations were the prevention of contamination during collection of the samples, and the stabilization of the two components prior to analysis.

The bottom sample was collected by lowering the CPE tubing to the prescribed depth, purging the system with estuarine water and allowing the same water sample to flow through the system for 30 minutes. The flow rate was a liter every 2 seconds, or 900 liters in the 30 minutes prior to collection. A 2-liter CPE bottle was rinsed three times with the sample, and then the sample was collected and capped. It took four seconds to fill the collection bottle. The collection bottle was cleaned and rotated between samples, being used once every 4-5 days. It was cleaned between uses with 1:4 reagent grade HNO_3 and high purity water [23,24].

The filtration of the bottom sample was started while the upper water column sample was being obtained. The variety of loadings required the use of one, two, or three filters depending on the solids content of each liter filtered. The sample bottle with the 32 mL of NBS high purity HNO_3 was placed under the filter apparatus and filled to the bottle rim. Each bottle contained 1062.5 mL, with 0.29% relative uncertainty (2s) between 12 bottles. This was done in duplicate to provide a separate particulate filter for both GFAA and NAA. The second bottle of filtered sample was unacidified and used to determine density, using a close range hydrometer and thermometer, and then discarded. The two sets of filters were placed in plastic filter holders and labeled. The acidified bottle containing the aqueous sample was placed in a CPE polyethylene bag sealed and stored in a wooden chest for transport.

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While the sample was being filtered, another member of the team retracted the bottom sampler, and the surface sampler was attached, as described, using the PVC disconnect. The sampler was lowered to approximately 1 ± 0.3 meters, as described, and the sample was pumped for 10 minutes at a rate of 1 liter/2 seconds, until 300 liters of sample had passed through the system. Two liters of the surface sample were collected using the same technique discussed for the bottom sample. The same filtration procedure was applied immediately upon collection. Prior to shutting down the sampling system, the system was backflushed with NBS deionized-distilled water to flush the pump and valves and then closed off by the valves.

An outline of the sampling procedure is shown in Figure 3, and an overview of the sample division is shown in Figure 4.

COLUMN SEPARATION APPARATUS

The Isolab QS-Q polypropylene column with porous polyethylene resin support was used with the QS-S 25-mL conventional polyethylene extension funnel attached to the column to act as a reservoir for the samples.

QUALITY ASSURANCE

NBS SRM 1643a was used as a quality assurance check on the chemistry separation preconcentration and on the instrumental methods. This material is a synthetic water standard designed to approximate a filtered and acidified fresh water sample. The concentrations of 17 elements have been certified by NBS, using two or more independent analytical techniques or a reference method of known accuracy [25,26]. The chemical preparation of these standards were identical to the Chesapeake Bay samples and they were dispersed among the analyses of the dissolved samples.

COLUMN PREPARATION AND PURIFICATION PROCEDURE

The polypropylene chromatographic columns, used to hold the Chelex 100 resin, were soaked for one week in 4 M HNO_3 and one week in 3 M HCl before use. After rinsing with water, a slurry corresponding to 3.2-3.4 mL of hydrated resin in the sodium form (about 400 mg dry weight) was loaded into each column. The resin was washed with three 5-mL portions of 2.5 M HNO_3 to elute any trace metal contamination. Excess acid was removed by washing the resin with two 5-mL volumes of high purity water. The resin was transformed to the NH_4+ form by the addition of two 5-mL volumes of 2.0 M NH_4OH. The pH of the last few drops eluted was checked using pH paper. If they were not basic, additional NH_4OH was added until basicity was achieved. Residual NH_4OH was removed from the resin with two 5-mL water washes.

SEPARATION PROCEDURE

The seawater samples, which had been filtered and preserved with HNO_3, were adjusted to a pH range of 5.2-5.7 by dropwise addition of NH_4OH. A few drops of 8 M ammonium acetate was then added to aid in buffering the system. A small amount of the sample was added to the column to allow the resin to undergo its normal shrinkage as it changes in pH and ionic form. The 25-mL

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Water Sampling Procedure Outlined

Lower tubing to depth minus one meter

Purge sampler of air using Bay water

Sample pumped continuously for 30 minutes at 1 liter/2 sec

2 liter sample collected in clean thrice purged polyethylene

Sample commenced filtration within minutes

Surface sampler connected in place of bottom sampler

Surface water pumped for 10 minutes at 1 liter/2 sec

2 liter sample collected in clean thrice purged polyethylene

Sample commenced filtration within minutes

Sampler back flushed with high purity water prior to shutdown

Figure 3.

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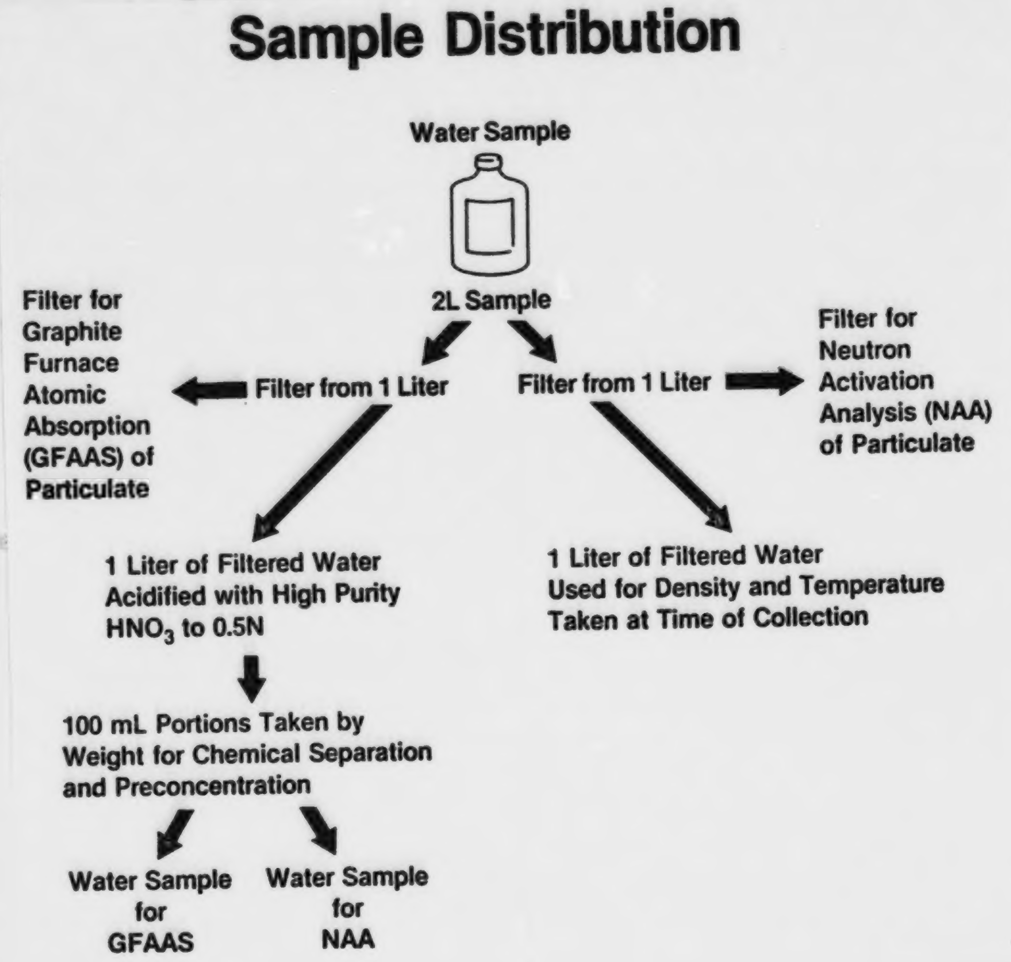
Sample Distribution
Water Sample
2L Sample
Filter from 1 Liter
Filter from 1 Liter
Filter for Graphite Furnace Atomic Absorption (GFAAS) of Particulate
Filter for Neutron Activation Analysis (NAA) of Particulate
1 Liter of Filtered Water Acidified with High Purity HNO3 to 0.5N
1 Liter of Filtered Water Used for Density and Temperature Taken at Time of Collection
100 mL Portions Taken by Weight for Chemical Separation and Preconcentration
Water Sample for GFAAS
Water Sample for NAA

Figure 4.

polyethylene reservoir atop the column was then filled, and the sample passed through the resin at a flow rate of about 0.8 mL/min. After the sample had passed through the resin, the resin was washed twice with 5 mL of water, and four 10-mL volumes of 1.0 M ammonium acetate were added to selectively elute the alkali and the alkaline earth metals. Residual ammonium acetate was removed with two 5-mL water washes.

At this point, the preparation of the aqueous samples diverged. For NAA, the resin was air dried in the column under a class 100 clean air facility and transferred to an acid-washed, 0.025-mm (1 mil) linear polyethylene (LPE) bag. This bag was heat sealed and sealed within a second bag made of 0.10-mm (4 mil) CPE, to prevent contamination during handling and irradiation. LPE was used for the inner bags, due to its lower blank levels (compared to CPE),

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while the outer bags were made of CPE, due to the greater flexibility of this material after neutron irradiation. Although LPE is, in general, stronger than CPE, it becomes brittle after long irradiations and has a tendency to crack. For GFAA, the transition metals were eluted using 7 mL of 2.5 M HNO_3 and collected into clean, preweighed 10-mL conventional polyethylene bottles. The bottles were capped with clean polyethylene-lined caps and reweighed to determine the weight of the effluent accurately.

STANDARDS

Two types of multielemental standards for NAA were used. The first type was prepared by pipetting known amounts of multielemental solutions onto 5.5-cm Whatman 41 filters. The filters were air-dried, pelletized, and doubly sealed in polyethylene bags [27]. The second type was prepared by pipetting standard solutions directly into LPE bags containing approximately 400 mg of dry Chelex 100 resin in the ammonium form, which had been prepared using the column preparation procedure previously described. The resin was allowed to dry at room temperature under class 100 conditions, after which the bags were sealed and placed within second CPE bags. Molybdenum and uranium were in separate standards, since significant amounts of ^{99}Mo are produced from uranium fission.

IRRADIATION AND COUNTING PARAMETERS FOR NAA OF DISSOLVED SAMPLES

The sealed samples (10-12) were packaged for irradiation with standards and blanks, and occupied two levels within the polyethylene irradiation container (rabbit). Each rabbit was irradiated for 4 hours in the RT-3 pneumatic tube facility of the NBS reactor. This facility has a thermal neutron flux of $5 \cdot 10^{13} n \cdot cm^{-2} \cdot s^{-1}$ [28]. Midway through the irradiation the rabbit was removed from the reactor, flipped end-over-end, and reinserted into the reactor to compensate for the linear neutron flux drop-off. After appropriate decay intervals the samples were counted with Ge(Li) and Ge(HP) detectors having active volumes of 60-90 cm^3. A Nuclear Data ND6620 computer-based analyzer system was used for data collection and reduction. A more detailed description of this analytical method can be found in Appendix 2.

IRRADIATION AND COUNTING PARAMETERS FOR NAA OF PARTICULATE SAMPLES

The samples, consisting of one, two, or three filters, were folded and sealed in two cleaned, 0.025-mm (1 mil) LPE bags. The samples and standards (solutions pipetted onto Whatman 41 filters) were irradiated at the University of Missouri reactor for 2-3 hours at a thermal neutron flux of 5.9×10^{13} $n \cdot cm^{-2} \cdot s^{-1}$. After decaying for several days, the samples were shipped back to NBS, where the outer bags were removed and the samples were counted 4 cm from the detector. A Gamma-X detector, coupled to 8192 channels of computer memory, was required to measure Zn, due to the proximity of the Zn peak at 1115 keV and the much larger Sc peak at 1120 keV. The Nuclear Data ND6620 was used for data collection and reduction. Each standard, as well as some of the samples, was counted twice to check the reproducibility of counting position and the decay corrections calculated by the computer.

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DETERMINATION OF DISSOLVED FRACTION BY GFAA

The estuarine samples from the Chesapeake Bay were preconcentrated using the method described by Kingston and Rains, et al. [1]. The eluate from this separation (contained in 2.5 M HNO_3) was analyzed directly for the Cd, Cu, Mn, Ni and Pb by GFAA, using the L'vov platform. To check for chemical interferences, the single standard addition method was used [29]. The instrumental conditions for each element are given in Table 1. A more detailed description of these methods can be found in Appendices 3 and 4.

DETERMINATION OF PARTICULATE FRACTION BY GFAA

The solids which were collected on 0.45 µm filters were prepared by transferring each filter to a Teflon beaker. Then, 5 mL of HNO_3 and 1 mL of HF were added and solution warmed. After the paper had decomposed, 5 mL of $HClO_4$ was added and sample solution evaporated to near dryness. The solids were then dissolved in 1 mL of HNO_3 and 5 mL of water and then transferred to 10 mL volumetric flask. The analytes were determined by GFAA, using the instrumental conditions described in Table 1. The recovery of each analyte was checked by the single addition method [29]. A more detailed description of these parameters can be found in Appendix 4 and reference [1].

PROCEDURAL BLANK PREPARATION

A total of 30 sets of blanks were prepared on the ship during the processing of the samples. Each set consisted of a dissolved fraction, and a particulate fraction (filter). They were prepared using bottles from the same lot which were cleaned at the same time and contained subboiled distilled NBS high-purity water. The blanks were opened for 20 seconds on the deck, prior to manipulation, to simulate as closely as possible the actual samples. This water was passed through the same lot number of Amicon and Millipore filters, either one, two, or three filters in the same apparatus, using the same conditions and done in between actual samples. The blanks acidified from the same container of NBS acid was stored under the same conditions as the samples. They were carried through all operations as if they were actual samples and analyzed with the samples to determine the total analytical blank.

We were unable to evaluate any blank contribution from the pumping system, since a single sampling blank would require approximately 1000 liters of high-purity water (∿$100 per liter) to follow the same procedure which was used for the samples. However, in view of the non-contaminating components of this system (all plastic), the large volume of water used to flush the system prior to sample collection, and the rapid flow rate through the system during sample collection any blank contribution should be negligible.

ANALYTICAL BLANK CORRECTION AND DATA ADJUSTMENT

Each element of each type of sample particulate and dissolved was modeled for blank correction. Each element blank set was modeled, and the resulting model was used for the blank correction. The concentration is given as a point estimate and as an interval estimate. The interval estimates

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TABLE 1. INSTRUMENTAL PARAMETERS FOR GFAA ANALYSIS

	-- P & E 603 --				----------- HGA - 2200[a] ----------		
Element	Wavelength nm	SBW nm	Scale Expansion	Gas	Drying[c] T - sec	Charring[c] T - sec	Atomization T - sec
Cd[b]	228.8	0.7	2	Ar	125 - 40	800 - 40	2300 - 6
Cu	324.7	0.7	2	Ar	125 - 40	700 - 40	2600 - 6
Mn	279.5	0.7	2	Ar,Stop Flow	125 - 40	800 - 40	2700 - 6
Ni	232.0	0.7	5	Ar	125 - 40	800 - 40	2700 - 6
Pb[b]	283.3	0.7	3	Ar	125 - 40	800 - 40	2400 - 6

[a] With L'vov Platform.

[b] $(NH_4)_2\ HPO_4$ used in matric modification.

[c] Ramp mode used for first 20 seconds.

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are approximately at the 95% confidence level. The raw data were computerized, and a set of conditions and blank influences for each element of each sample type was submitted to the Chesapeake Bay EPA computer for adjustment into final form. Both blank influence and statistical uncertainty were adjusted by the computer through this series of individual elemental models.

The statistical considerations for each element are set forth in Appendix 5 [30].

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RESULTS AND DISCUSSION

The purpose of this report is to present the elemental concentration data and describe the methodology used in its acquisition. These results will be used in combination with other studies to assess the current state of the Chesapeake Bay. The efforts utilized can be described as the best available technology with modifications (within fiscal scope) to achieve the maximum information available for each sample. Each concentration determination was done by the analyst having only numbered samples with no reference as to the location or relationship of one sample to another. In all, 15 elements were analyzed (Ce only in particulates) in 102 samples (plus blanks and standards) of dissolved and particulate estuarine samples from the Chesapeake Bay. The physical site and sample characteristics are described in Appendix 1. The range of concentrations covered between four and five orders of magnitude for some elements.

As one means of quality control, trace elements in water (NBS Standard Reference Material 1643a) was treated as a sample and analyzed in conjunction with the dissolved water samples. The results of these analyses are presented in Tables 2 and 3. Additionally, both NAA and GFAAS techniques analyzed certain elements in common, such as Ni.

— T. 2 + 3

TABLE 2. TRACE ELEMENTS IN WATER — SRM 1643a ANALYZED USING CHELATION AND NAA

Element	Concentration -- ng/g This Work[a]	 Certified
Cd	10.1 ± 0.5	10 ± 1
Co	19 ± 1	19 ± 2
Cr	16 ± 2	17 ± 2
Cu	19.1 ± 0.6	18 ± 2
Fe	88 ±16	88 ± 4
Mn	30.9 ± 0.6	31 ± 2
Mo	97 ± 6	95 ± 6
Ni	56 ± 8	55 ± 3
V	52 ± 1	53 ± 3
Zn	68 ± 5	72 ± 4

[a] Uncertainties are 2s.

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TABLE 3. TRACE ELEMENTS IN WATER — SRM 1643a ANALYZED USING CHELATION AND GFAA

Sample	Pb	Ni	Cu	Cd
	ng/mL			
TWS -1	33	--	16, 19 17, 18 17, 19	12
-2	26 28	--	--	11
-3	27	--	14	10
-4	27 26 27	56	13	13
-5	27 31 27	--	13	11
-6	27 29	49 53 48	14 16	--
Average =	28	52	16	11
2s =	4	7	4	2
Certified Values =	27 ± 1	55 ± 3	18 ± 3	10 ± 1

The extremely low trace concentrations in these estuarine waters caused the procedural blank to be of paramount importance. The integrity of the sample can be compromised by just a brief exposure to normal laboratory air or less than exhaustively cleaned container materials, etc. In addition, the extremely high concentrations of alkali, alkaline earth, and halogen elements in the marine water matrix make direct analysis difficult or impossible for most analytical techniques.

To circumvent these problems, special chemical and instrumental procedures were developed and chemical separation/preconcentration procedures based on the chelating resin Chelex-100 were applied prior to NAA and GFAAS analysis [1,2]. The elimination of the matrix elements allowed the determination of many elements which could not otherwise be analyzed and enhanced the sensitivity of other elements of interest. The control of the blank in this procedure has enabled its contribution to be sufficiently low that it did not limit the measurement of most elements in pristine samples.

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While many elements appeared to be free of any blank contribution, other elements have a blank contribution which was found to be significant. The particulate blank for zinc and chromium was contributed largely by both types of filters used, Amicon and Millipore (0.45 micrometer). The chromium was found to be significantly different between the two brands of filters, while the zinc was indistinguishable between brands (see figures 1 and 2 of Appendix 5). Attempts to preclean the filters proved ineffectual. Some apparatus, as exemplified by the filters, is unavoidably the limiting factor in the blank; available technology is in some cases the limiting factor due to the level of the analytical blank for specific elements. It is necessary to develop more specialized methodologies to achieve the lower levels of other elements frequently below detectable limits. Analysis of most of the elements were achievable with the available technology. Analytical procedures extensively utilized included clean laboratory chemistry, high sensitivity instrumental methodologies and rigorous statistical analysis of the determinable blank. Certain advances and refinements in techniques were achieved in preparation for and during this study. Rather than reiterate the more thorough discussions of each analytical technique used in the analysis of these samples, the specifics of these techniques have been placed in the appendices where they are described in detail (Appendices 2, 3, 4, and 5).

The concentration data are presented in tables collected in Appendix 6. The data for both the dissolved and particulate elemental concentrations are presented in Tables 1 through 29.

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To ensure sample integrity and accurate analytical blank determinations, thirty dissolved and particulate blanks were prepared during the sample collection. The blanks were then carried through all manipulations and analyses as additional samples interspersed throughout the analyses, with a minimum of three per set. These blanks have been included in Tables 30 through 58 of Appendix 6. They have undergone rigorous statistical scrutiny and their influence on the concentration measurements is discussed specifically in Appendix 5. Two components which it was not possible to determine in the blank are the sampling blank and the high-purity water used to make up the blanks.

We were unable to evaluate any blank contribution from the pumping system, since a single sampling blank would require approximately 1000 liters of high-purity water (~$100 per liter, if that much of this reagent could be obtained) to follow the same procedure which was used for the samples. However, in view of the non-contaminating components of this system (specific plastics), the large volume of sample water used to flush the system prior to sample collection, and the rapid flow rate through the system during sample collection this blank contribution should be negligible. Thus it is possible for a sampling system component to the blank to exist for one or more elements underlying the other sources of blank.

A second contribution to the blank which could not be determined was that of the high-purity water used to make the blanks. The water is, for the elements of interest, lower in these elements than the levels being analyzed [21]. Since the high-purity water is not part of the actual samples any contribution from the high-purity water used would raise the observed

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blank higher than it actually exists in the real samples. This then can only contribute to an over estimation of the real blank.

Although several blanks are undetectable others have been, in many cases, traced to the filters or specific processes as described in Appendix 5. The uncertainty in the concentration data take into account the uncertainty in the blank as well as the instrumental uncertainties.

Some understanding of the dissolved elemental concentrations can be gained by comparing the concentrations to normal seawater values (Appendix 2). Most marine organisms can be expected to tolerate the naturally occurring levels of toxic elements reasonably well. However, concentration data does not give an indication of the origins of each element or its chemical interactions. Even the extent of the influence of the ocean versus fresh water in each sample can not be evaluated by studying the elemental concentrations alone. It is only with a coordinated comparison of elemental concentration with density and other characteristic elemental concentrations that contributions and origins can be understood and logical hypotheses be verified.

These evaluations are possible using computer assisted statistical comparisons with data of known statistical reliability. The analysis, blank contribution, corrections and mathematical manipulation of the data in this report have resulted in 58 data sets which are of known statistical reliability. These data sets contain the sample numbers arranged in a numerical sequence approximating the geological arrangement of the Chesapeake Bay, from the Susquehanna River to and including the Atlantic Ocean. The concentrations are given as a best value, and a maximum and minimum value which represents at least the 95% confidence limit of the concentration. The significant figures of each concentration are determined by the range of the maximum and minimum value.

The potential information in the particulate elemental concentration data is even more difficult to understand. The concentrations obtained were in elemental mass (ng) per unit volume (mL) of water. The total amount of particulate mass suspended at the time of sample collection strongly affects the results. Variations in current, tide, temperature, biota, wind conditions, etc. can greatly influence the total amount of particulate material suspended in the water column. The total mass collected is not a direct indication of the amount of suspended inorganic particulate matter. The total mass is most profoundly affected by the amount of salt remaining on the filter and the amount of organic matter frequently in the form of plankton or algae residing with it. In most cases the concentration of the elements of interest would be much higher in the bottom sediments than in the biological material.

Although the particulate data may appear initially to be uncertain in interpretive value, a technique long used in the study of atmospheric particulate material is applicable [30,31]. The comparison of elemental ratios for different samples instead of the absolute concentration is informative. By normalizing the concentration of each element to a crustal element, such as Sc, problems caused by differing amounts of bottom sediment suspended in water (loading effects) are eliminated.

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Scandium was chosen for this purpose because it has relatively few anthropogenic uses. Since it is not used in a refined form in industry and is refractory in nature, it is not expected to be introduced into the environment in an enriched state or in significant quantities. When these ratios are divided by ratios of average crustal material, a crustal enrichment factor (EF) results. This is done for convenience and also to allow a crude comparison with naturally occuring material. For example the elemental concentration in proposed NBS SRM 1646, an estuarine sediment collected in the Chesapeake Bay were transformed into EFs in Table 5.

TABLE 5. ELEMENTAL CONCENTRATIONS AND CRUSTAL ENRICHMENT FACTORS FOR PROPOSED ESTUARINE SEDIMENT SRM 1646

	Concentration in µg/g or %	Enrichment Factors	
Li	49	2.08	
Na	2.0%	1.04	
K	1.4%	0.63	
Rb	85	0.90	
Cs	3.6	1.70	
Mg	1.09%	1.00	
Ca	0.83%	0.37	
Al	6.25	1.02	
Si	31%	1.29	
Sc	10.7	1.00	
V	88	1.18	
Cr	76	1.38	
Mn	375	0.69	
Fe	3.35%	1.20	
Co	10.1	1.07	
Ni	32	0.93	
Cu	18	0.76	
Zn	138	2.93	
Cd	0.36	4.58	Soils = 0.47*
Sb	0.43	2.74	Sed. Rock = 1.12
Ce	79	1.34	
Eu	1.5	1.36	
Th	9.9	1.15	
Hg	0.063	2.67	
Pb	28.2	2.39	

*Enrichment factors relative to average soils and sedimentary rocks [33].

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In these data the concentrations from Wedepohls' compilation [32] for crustal elements has been used. Similar though not identical results could be obtained using other compilations. Additionally the computation of EFs relative to average soils and average sedimentary rocks would be of value to see how the suspended sediments of the Chesapeake Bay differ from these natural materials. The cadmium enrichment factors relative to average sedimentary rock and average soils [33] are given as examples in Table 5.

Enrichment factors can also be used to identify significant inputs of material to the Bay. The EF of an element being added to the Bay in significant quantity from a refined source should be higher near the source and decrease with distance.

Ideally the EFs for each element will remain constant if the sources contributing to the suspended sediment remain the same. Although the concentration of the various elements may fluctuate several orders of magnitude from sampling to sampling, the EFs should be constant if the sources are constant as they are not effected by mass loading.

As an example of this theory, the comparison of Sc with another relatively nonanthropogenic element, Ce, is instructive. The concentration ranges of Ce and Sc are between two and three orders of magnitude. The range of the enrichment factors, however, was just 45% of the mean value and the relative standard deviation was only 10%. No additional variability over the analytical uncertainties were observed. Not only were the analytical uncertainties contained within these limits but the total natural inhomogeneity of the environmental ratios for the entire estuary was also contained within this range. It is instructive to recall that this study geographically included samples of river waters from the Susquehanna, through its range of mixing, to the Atlantic Ocean beyond the confines of the Chesapeake Bay with both the top and bottom of the water column sampled at each of the 51 locations. Before an interpretive value can be hypothesized for the enrichment factors calculated from the particulate data, control of the system must be demonstrated. While this example is not an exhaustive establishment of control it is extremely significant from an analytical measurement and systems behavior perspective. This type of correlation reliability is rare in environmental data.

Uses of these EFs to produce an interpretive model for evaluating and concluding elemental relationship and origins can be postulated. However, actual conclusions cannot be drawn until a rigorous scrutiny of the statistical significance of the individual sets of enrichment factors has been completed. Because this technique has not been used for water particulates previously, many cross references between elements and geological positioning, as well as within set limits, must be evaluated.

In this report the enrichment factors normalized to the Wedepohl crustal numbers have been given without interpretation to at least the 90% confidence limit. These values for the particulates are presented in Tables 59 through 72 of Appendix 6.

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These data are of sufficiently well known reliability that statistical comparison can be performed resulting in significant trends of known reliability. This work has not been included in this report and is of a sufficiently complex nature to comprise a separate effort. This effort has been recently initiated.

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LITERATURE CITED

[1] Kingston, H. M., Barnes, I. L., Brady, T. J., Rains, T. C., Champ, M. A. Anal. Chem. , 1978, 50, 2064.

[2] Greenberg, R. R., Kingston, H. M. J. Rad. Chem., 1981, in press (see Appendix 2).

[3] Kingston, H. M., Pella, P. A. Anal. Chem., 1981, 53, 223.

[4] Leyden, D. E., Patterson, T. A., Alberts, J. J. Anal. Chem., 1975, 47, 733.

[5] Goldbert, E. D. "Marine Pollution Monitoring: Strategies for a National Program", NOAA, Washington, DC, 1972.

[6] Lee, C., Kim, N. B., Lee, I. C., Chung, K. S. Talanta, 1977, 24, 241.

[7] Stephens, B. G., Felkel, Jr., H. L., Spinelli, W. M. Anal. Chem., 1974, 46, 692.

[8] Zirino, A., Lieberman, S. H., Chapter in "Analytical Methods in Oceanography", T.R.P. Gibbs, Jr., Ed., Adv. Chem. Ser., 1975, 147.

[9] Sperling, K. R. At. Absorpt. Newsl., 1976, 15, 1.

[10] Paus, P. E. Fresenius. Z. Anal. Chem., 1973, 264, 118.

[11] Segar, D. A., Gonzalez, J. G. Anal. Chim. Acta, 1972, 58, 7.

[12] Fabricand, B. P., Sawyer, R. R., Ungar, S. G., Adler, S. Geochim. Cosmochim. Acta, 1962, 26, 1023.

[13] Riley, J. P., Skirrow, G. "Chemical Oceanography", Vol. III, Academic Press, New York, 1975.

[14] Burell, D. C. Anal. Chim. Acta, 1967, 38, 447.

[15] Kremling, K., Peterson, H. Anal. Chim. Acta, 1974, 70, 35.

[16] Riley, J. P., Taylor, D. Anal. Chim. Acta, 1968, 40, 479.

[17] Davey, E. W., Soper, A. E., Chapter in "Analytical Methods in Oceanography", T.R.P. Gibbs, Jr., Ed., Adv. Chem. Ser., 1975, 147.

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[18] Florence, T. M., Batley, G. E., *Talanta*, 1976, *23*, 179.

[19] Florence, T. M., Batley, G. E., *Talanta*, 1977, *24*, 151.

[20] Ediger, R. D., Peterson, G. E., Kerber, J. D. *At. Absorpt. Newsl.*, 1974, *13*, 61.

[21] Keuhner, E. C., Alvarez, R., Paulsen, P. J., Murphy, T. J. *Anal. Chem.*, 1972, *44*, 2050.

[22] Federal Standard 209b, Government Services Administration, Boston, Massachusetts, 1973.

[23] Moody, J. R., Lindstrom, R. M. *Anal. Chem.*, 1977, *49*, 2264.

[24] Maienthal, E. J., Becker, D. A. *Natl. Bur. Stand. (U.S.) Tech. Note*, 1976, *929*.

[25] Moody, J. R., Rook, H. L., Paulsen, P. J., Rains, T. C., Barnes, I. L., Epstein, M. S. *Natl. Bur. Stand. (U.S.) Spec. Publ.*, 1977, *464*, W. A. Kirchhoff, Ed.

[26] Natl. Bur. Stand. (U.S.) Certificate of Analysis, SRM 1643a, 1980.

[27] Greenberg, R. R. *Anal. Chem.*, 1979, *51*, 2004.

[28] Becker, D. A., LaFleur, P. D. *J. Radioanal. Chem.*, 1974, *19*, 149.

[29] Dean, J. A., Rains, T. C., eds., "Flame Emission and Atomic Absorption Spectrometry", Vol. 3, Marcel Dekker, New York, 1975.

[30] Gordon, G. E., Zoller, W. H., Proceedings 1st Annual NSF Trace Contaminants Conference, Oak Ridge, Tennesssee, pp. 314-325, August 1973.

[31] Gordon, G. E., Zoller, W. H., Gladney, E. S., Proceedings 7th Annual Conference on Trace Substances in Environmental Health, Columbia, Missouri, pp. 167-174, June 1973.

[32] Wedepohl, K. H., in *Origin and Distribution of the Elements*, L. H. Ahrens, ed., Pergamon Press, London, 1968, pp. 999-1016.

[33] Vinogradov, A. P., *The Geochemistry of Rare and Dispersed Chemical Elements in Soils*, The English translation, Consultants Bur., New York, 2nd edition, 1959.

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APPENDIX 1

APPENDIX 1

SITE AND SAMPLE CHARACTERISTICS

Station	No.	Location		Time of Sampling				Depth in			Filter No. &
NBS	MGS	Longitude	Latitude	Time	Month/Day/Year			Feet	Density[a]	Salinity[b]	Type
11102	0	76 18 34	39 15 24	17:45	July	6	1979	T	0.9995	3.21	3 M
11101	0	76 18 34	39 15 24	17:45	July	6	1979	018	0.9994	3.08	3 M
11100	1	76 4 28	39 32 60	13:30	July	5	1979	T	0.9978	0.95	1 M
11099	1	76 4 28	39 32 60	13:30	July	5	1979	025	0.9984	1.75	1 M
11098	53	76 0 17	39 27 25	:	July	5	1979	T	0.9978	0.95	2 M
11097	53	76 0 17	39 27 25	:	July	5	1979	022	0.9977	0.82	2 M
11096	51	75 59 18	39 30 17	12:00	July	4	1979	T	0.9980	1.22	3 M
11095	51	75 59 18	39 30 17	12:00	July	4	1979	011	0.9983	1.62	3 M
11094	2	76 2 38	39 24 49	8:45	July	4	1979	T	0.9979	1.08	2 M
11093	2	76 2 38	39 24 49	8:45	July	4	1979	010	0.9978	0.95	2 M
11092	6	76 23 39	39 9 1	15:30	July	3	1979	T	1.0014	5.74	3 M
11091	6	76 23 39	39 9 1	15:30	July	3	1979	019	1.0015	5.88	3 M
11090	8	76 19 2	39 5 54	9:00	July	3	1979	T	1.0012	5.48	2 M
11089	8	76 19 2	39 5 54	9:00	July	3	1979	023	1.0013	5.61	2 M
11088	54	76 27 41	38 49 5	15:30	July	2	1979	T	1.0027	7.48	2 M
11087	54	76 27 41	38 49 5	15:30	July	2	1979	100	1.0031	8.01	2 M
11086	55	76 23 38	38 48 50	12:00	July	2	1979	T	1.0028	7.61	2 M
11085	55	76 23 38	38 48 50	12:00	July	2	1979	105	1.0067	12.80	2 M
11084	56	76 21 22	38 49 0	7:45	July	2	1979	T	1.0033	8.27	2 M
11083	56	76 21 22	38 49 0	7:45	July	2	1979	048	1.0026	7.34	2 M
11082	13	76 29 34	38 39 5	6:30	July	1	1979	T	1.0035	8.54	3 M
11081	13	76 29 34	38 39 5	6:30	July	1	1979	025	1.0034	8.41	2 M
11080	14	76 25 45	38 39 16	15:15	June	30	1979	T	1.0036	8.67	2 A
11079	14	76 25 45	38 39 16	15:15	June	30	1979	041	1.0034	8.41	2 A
11078	15	76 18 48	38 39 21	0:15	June	30	1979	T	1.0032	8.14	3 A
11077	15	76 18 48	38 39 21	0:15	June	30	1979	020	1.0035	8.54	2 A
11076	57	76 24 17	38 25 44	8:00	June	30	1979	T	1.0046	10.01	2 A
11075	57	76 24 17	38 25 44	8:00	June	29	1979	037	1.0051	10.67	2 A
11074	58	76 21 25	38 25 50	:	June	29	1979	T	1.0042	9.47	2 A
11073	58	76 21 25	38 25 50	:	June	29	1979	081	1.0088	15.60	2 A
11072	59	76 19 39	38 25 57	:	June	29	1979	T	1.0042	9.47	2 A
11071	59	76 19 39	38 25 57	:	June	29	1979	022	1.0038	8.94	2 A
11070	61	76 16 56	38 11 13	:	June	29	1979	T	1.0043	9.61	2 A
11069	61	76 16 56	38 11 13	:	June	29	1979	042	1.0066	12.67	2 A
11068	60	76 19 38	38 11 19	:	June	29	1979	T	1.0043	9.61	2 A
11067	60	76 19 38	38 11 19	:	June	29	1979	033	1.0053	10.94	2 A
11066	62	76 13 41	38 11 15	:	June	29	1979	T	1.0051	10.67	2 A
11065	62	76 13 41	38 11 15	:	June	28	1979	097	1.0103	17.60	2 A
11064	63	76 8 14	38 11 40	:	June	28	1979	T	1.0050	10.54	2 A
11063	63	76 8 14	38 11 40	:	June	28	1979	023	1.0049	10.41	2 A
11062	64	76 57 53	38 12 18	8:30	June	28	1979	T	1.0042	9.47	3 A
11061	64	75 57 53	38 12 18	8:30	June	28	1979	024	1.0047	10.14	2 A
11060	25	76 7 35	38 59 27	10:00	June	27	1979	T	1.0042	9.47	2 A
11059	25	76 7 35	38 59 27	10:00	June	27	1979	025	1.0052	10.81	2 A
11058	24	76 12 44	38 0 0	6:00	June	27	1979	T	1.0033	8.27	2 A
11057	24	76 12 44	38 0 0	6:00	June	27	1979	044	1.0065	12.54	2 A
11056	23	76 17 25	38 0 0	18:30	June	26	1979	T	1.0031	8.01	2 A
11055	23	76 17 25	38 0 0	18:30	June	26	1979	B	1.0051	10.67	2 A
11054	21	75 58 18	38 4 55	12:00	June	26	1979	T	1.0047	10.14	2 A
11053	21	75 58 18	38 4 55	12:00	June	26	1979	030	1.0053	10.94	2 A
11052	65	75 55 36	37 58 18	9:00	June	26	1979	T	1.0056	11.34	2 A
11051	65	75 55 36	37 58 18	9:00	June	26	1979	088	1.0060	11.87	2 A

Appendix 1, Site and Sample Characteristics continued

Station NBS	No. MGS	Location Longitude	Location Latitude	Time of Sampling Time	Time of Sampling Month/Day/Year	Depth in Feet	Density	Salinity	Filter No. & Type
11050	76	75 57 3	37 53 50	:	June 24 1979	T	1.0053	10.94	2 A
11049	76	75 57 3	37 53 50	:	June 24 1979	095	1.0053	10.94	2 A
11048	78	75 55 33	37 50 55	:	June 24 1979	T	1.0067	12.80	2 A
11047	78	75 55 33	37 50 55	:	June 24 1979	078	1.0068	12.94	3 A
11046	80	75 58 5	37 46 53	13:15	June 23 1979	T	1.0053	10.94	3 A
11045	80	75 58 5	37 46 53	13:15	June 23 1979	060	1.0077	14.13	3 A
11044	81	75 51 41	37 45 36	9:30	June 23 1979	T	1.0069	13.07	2 A
11043	81	75 51 41	37 45 36	9:30	June 23 1979	B	1.0067	12.80	3 A
11042	85	76 4 27	37 41 1	6:30	June 23 1979	T	1.0064	12.40	2 A
11041	85	76 4 27	37 41 1	6:30	June 23 1979	033	1.0089	15.73	2 A
11040	84	76 7 56	37 40 20	17:30	June 22 1979	T	1.0052	10.81	2 A
11039	84	76 7 56	37 40 20	17:30	June 22 1979	042	1.0096	16.67	2 A
11038	77	76 7 58	37 52 1	14:00	June 22 1979	T	1.0044	9.74	2 A
11037	77	76 7 58	37 52 1	14:00	June 22 1979	057	1.0084	15.07	2 A
11036	79	76 10 46	37 49 31	10:45	June 22 1979	T	1.0051	10.67	2 A
11035	79	76 10 46	37 49 31	10:45	June 22 1979	055	1.0091	16.00	2 A
11034	82	76 11 29	37 45 8	8:30	June 22 1979	T	1.0057	11.47	2 A
11033	82	76 11 29	37 45 8	8:30	June 22 1979	075	1.0100	17.20	2 A
11032	83	76 13 17	37 41 35	14:30	June 21 1979	T	1.0052	10.81	3 A
11031	83	76 13 17	37 41 35	14:30	June 21 1979	041	1.0080	14.53	2 A
11030	87	76 10 38	37 31 23	10:30	June 21 1979	T	1.0064	12.40	2 A
11029	87	76 10 38	37 31 23	10:30	June 21 1979	030	1.0099	17.06	2 A
11028	86	75 55 0	37 38 44	7:15	June 21 1979	T	1.0044	9.74	2 A
11027	86	75 55 0	37 38 44	7:15	June 21 1979	055	1.0050	10.54	3 A
11026	88	76 7 52	37 25 39	13:00	June 20 1979	T	1.0080	14.53	2 A
11025	88	76 7 52	37 25 39	13:00	June 20 1979	034	1.0126	20.66	2 A
11024	89	76 1 3	37 24 13	:	June 20 1979	T	1.0107	18.13	2 A
11023	89	76 1 3	37 24 13	:	June 20 1979	046	1.0091	16.00	2 A
11022	90	76 10 26	37 22 7	9:30	June 20 1979	T	1.0079	14.40	2 A
11021	90	76 10 26	37 22 7	9:30	June 20 1979	024	1.0090	15.87	2 A
11020	93	76 10 56	37 18 50	:	June 19 1979	T	1.0071	13.34	3 A
11019	93	76 10 56	37 18 50	:	June 19 1979	040	1.0090	15.87	3 A
11018	92	76 21 34	37 20 26	10:30	June 19 1979	T	1.0085	15.20	3 A
11017	92	76 21 34	37 20 26	10:30	June 19 1979	014	1.0085	15.20	3 A
11016	94	76 6 11	37 19 3	7:05	June 15 1979	T	1.0085	15.20	2 A
11015	94	76 6 11	37 19 3	7:05	June 15 1979	053	1.0132	21.46	2 A
11014	91	76 1 6	37 21 31	13:30	June 14 1979	T	1.0108	18.26	1 A
11013	91	76 1 6	37 21 31	13:30	June 14 1979	B	1.0110	18.53	2 A
11012	97	76 3 54	37 14 19	9:30	June 14 1979	T	1.0123	20.26	2 A
11011	97	76 3 54	37 14 19	9:30	June 14 1979	110	1.0139	22.39	2 A
11010	96	76 7 9	37 10 49	7:00	June 14 1979	T	1.0110	18.35	2 A
11009	96	76 7 9	37 10 49	7:00	June 14 1979	024	1.0118	19.60	2 A
11008	100	75 54 53	36 55 46	14:00	June 13 1979	T	1.0156	24.66	1 A
11007	100	75 54 53	36 55 46	14:00	June 13 1979	065	1.0194	29.72	1 A
11006	98	76 03 06	37 01 15	8:30	June 13 1979	T	1.0035	8.54	2 A
11005	98	76 03 06	37 01 15	8:30	June 13 1979	060	1.0064	12.40	3 A
11004	99	76 13 58	37 0 32	16:00	June 12 1979	T	1.0082	14.80	3 A
11003	99	76 13 58	37 0 32	16:00	June 12 1979	055	1.0103	17.60	3 A
11002	95	76 16 38	37 12 46	0:01	June 12 1979	T	1.0099	17.06	2 A
11001	95	76 16 38	37 12 46	0:01	June 12 1979	035	1.0091	16.00	2 A

NOTE: T Depth = top sample (described in experimental section); NBS = National Bureau of Standards sample number; MGS = Maryland Geological Survey site number; Density = 25 °C; Filter = 1, 2, or 3 — the number of filters used for a 1 liter sample, A or M — Amicon or Millipore 0.45 micrometer filters were used.

[a] Uncertainty ±0.0002

[b] Calculated from density; supplied by EPA

APPENDIX 2

Greenberg and Kingston (1981), in press

SIMULTANEOUS DETERMINATION OF TWELVE TRACE ELEMENTS IN ESTUARINE AND SEAWATER USING PRE-IRRADIATION CHROMATOGRAPHY

R. R. Greenberg and H. M. Kingston
Center for Analytical Chemistry
National Bureau of Standards
Washington, D. C. 20234

Introduction

The considerable difficulty of trace element analysis in a high salt matrix such as seawater, estuarine water, or brine is clearly reflected in the literature. The extremely high concentrations of the alkali metals, the alkaline earth metals, and the halogens, combined with the extremely low levels of the transition metals and other elements of interest, make direct analysis by most analytical techniques difficult or impossible. Typical elemental concentrations in seawater [1] are listed in Table 1.

The use of a separation and/or preconcentration procedure prior to analysis is usually required. Riley and Skirrow have reviewed many of the alternative separation and preconcentration techniques employed to eliminate the matrix and/or concentrate the trace elements from a high-salinity material [1]. One of the prominent methods of seawater preconcentration uses the chelating resin Chelex-100*. Early Chelex-100 procedures, however, only partially separated the alkali and alkaline earth metals prior to the analysis of the eluted elements of interest [2-5].

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*Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

A more recent separation procedure utilizing the Chelex resin produced a sample devoid of alkali, alkaline earth, and halogen elements, and left a dilute nitric acid/ammonium nitrate matrix containing only the trace elements of the seawater sample [6]. While this procedure produces a highly desirable and appropriate matrix for most spectroscopic methods of analysis, a solid sample would be more appropriate for other instrumental techniques [7] such as x-ray fluorescence (XRF) or neutron activation analysis (NAA). In addition, the above separation procedure also makes it difficult or impossible to analyze several elements which are held strongly by the resin but cannot be quantitatively eluted. Chromium and vanadium exhibit this type of behavior, and attempts to reproducibly elute these elements from Chelex-100 have not been successful.

Neutron activation analysis has the inherent sensitivity and accuracy to determine a number of important trace elements in seawater at their naturally occurring levels. Unfortunately, a salt water matrix is not well suited for activation analysis. The use of liquid samples limits both the amount of material and the length of irradiation available in most reactor facilities. The high levels of Na, Cl, and Br produce an extremely high background level of radiation that totally obscures the signals of most elements whose neutron activation products have comparable half-lives.

This paper will describe a method to prepare solid samples from 100 mL of estuarine or seawater, using Chelex-100 resin, followed by the determination of 12 trace elements by NAA. Using this procedure, typical decontamination factors of $\geq 10^7$ for Na, $\geq 10^5$ for Cl, and $\geq 10^3$ for Br are observed. This procedure has been used to analyze NBS Standard Reference Material 1643a (Trace Elements in Water) as well as high salinity water samples collected near the mouth of the Chesapeake Bay.

Although one of the major advantages usually associated with NAA is the possibility of post-irradiation chemistry thus eliminating the problems associated with reagent blank and other types of contamination, the use of pre-irradiation chemistry for high-salinity waters has significant advantages. The removal of Na, Cl, and Br greatly reduces the background level of radiation during short and intermediate counts, and allows the determination of elements not otherwise possible without some type of separation. The removal of the matrix elements also greatly reduces the radiation dose received by personnel, especially if radiochemistry is used. The preconcentration of 100 mL of liquid to a sample of less than 0.5 gram increases the sensitivities for most elements and allows more samples to be irradiated within a single rabbit. Although other, non-chemical, concentration steps, such as lyophilization, could be employed prior to irradiation, they are relatively difficult to use with high salinity water, they leave the salts with the elements of interest, and they can also increase the blank from the equipment used, as well as from the material used to contain the sample. Finally, the use of Chelex-100 prior to irradiation produces a solid sample which eliminates the problems of storage, irradiation, and handling liquid samples.

Even without pre-chemistry, the number of sample manipulation steps required before the irradiation of a high salinity water sample is considerable including: collection; filtration; stabilization (usually by acidification); storage and encapsulation for irradiation. Extreme care during all these steps is necessary to prevent contamination of the samples. Extending the pre-irradiation treatment to include the Chelex-100 concentration/separation step produces significant benefits for the small additional effort required.

Experimental

Reagents. High purity water, nitric and glacial acetic acids were prepared using subboiling distillation at the National Bureau of Standards (NBS) [8]. All reagents used in the separation process were prepared in this manner and stored in clean FEP Teflon bottles unless otherwise stated.

Ammonium hydroxide was prepared by bubbling filtered ammonia gas through high purity water until room temperature saturation was achieved.

A 1.0M ammonium acetate solution was prepared by mixing 60 g of purified glacial acetic acid and 62 g of saturated NH_4OH and diluting to 1 L in a polypropylene volumetric flask. The acidity was adjusted to a pH range of 5.1 to 5.4 by dropwise addition of acetic acid and/or NH_4OH. All reagent and sample preparations were done in a class 100 clean air laboratory [9].

Chelex-100 chelating resin, 200-400 mesh size, was purchased from Bio-Rad Laboratories.

Column Separation Apparatus. The Isolab QS-Q polypropylene column with porous polyethylene resin support was used with the QS-S 25-mL conventional polyethylene extension funnel attached to the column to act as a reservoir for the samples.

Samples. Approximately 160 liters of high-salinity, estuarine water were obtained during high tide at the Virginia Institute of Marine Science (VIMS), Gloucester Point, Va., located near the mouth of the Chesapeake Bay. The sample was collected with a submersible pump and plastic tubing permanently submerged approximately 100 m offshore from the Institute [6]. The seawater was pumped directly into a conventional polyethylene drum which had been cleaned first with hydrochloric and then with nitric acid and purified water prior to use [10]. After filtration through a 0.45-μm millipore filter using an all polypropylene filter apparatus, the seawater was collected in a polyethylene carboy and acidified (to 0.6M in HNO_3) with high purity HNO_3 to prevent bacterial growth [6], to stabilize the trace element concentrations [11,12], and to strip any trace elements bound by colloidal particles [4,5].

Aliquots of this stabilized sample have been previously analyzed by graphite furnace atomic absorption spectrometry (GFAAS) [6], x-ray fluorescence spectrometry (XRF) [7], and isotope dilution mass spectrometry (IDMS) [13]. Each of these analytical techniques employed a separation/concentration step prior to analysis.

National Bureau of Standards-Standard Reference Material 1643a (Trace Elements in Water) was used to represent a low salinity water sample. This material is a synthetic water standard designed to approximate a filtered and acidified fresh water sample. The concentrations of seventeen elements have been certified by NBS using two or more independent analytical techniques, or a reference method of known accuracy [12,14].

Separation Procedure. The polypropylene chromatographic columns, used to hold the Chelex-100 resin were allowed to soak for one week in 4M HNO_3 and one week in 3M HCl before use. After rinsing with water, a slurry corresponding to 3.2-3.4 mL of hydrated resin in the sodium form (about 400 mg dry weight), was loaded into each column. The resin was washed with three 5 mL portions of 2.5M HNO_3 to elute any trace metal contamination. Excess acid was removed by washing the resin with two 5 mL volumes of water. The resin was transformed to the NH_4^+ form by the addition of two 5 mL volumes of 2.0M NH_4OH. The pH of the last few drops eluted was checked using pH paper. If they were not basic, additional NH_4OH was added until basicity was achieved. Residual NH_4OH was removed from the resin with two 5 mL water washes. The seawater samples, which have been filtered and preserved with HNO_3, were adjusted to a pH range of 5.2 - 5.7 by dropwise addition of NH_4OH. A few drops of 9M ammonium acetate was then added to aid in buffering the system. A small amount of the sample was added to the column to allow the resin to undergo its normal shrinkage as it changes in pH and ionic form. The 25 mL polyethylene reservoir atop the column was then filled and the sample passed through the resin at a flow rate of about 0.8 mL/min. After the sample had passed through the resin, the resin was washed twice with 5 mL of water, and four 10 mL volumes of 1.0M ammonium acetate were added to selectively elute the alkali and the alkaline earth metals. Residual ammonium acetate was removed with two 5 mL water washes. The resin was then air dried in the column under a class 100 clean air facility and transferred to an acid-washed, 0.025 mm (1 mil) linear polyethylene (LPE) bag. This bag was heat sealed, and sealed within a second bag made of 0.075 mm (3 mil) conventional polyethylene (CPE), to prevent contamination during handling and irradiation. Linear polyethylene was used for the inner bags due to its lower blank levels (compared to CPE), while the outer bags were made of CPE due to the greater flexibility of this material after neutron irradiation. Although LPE is in general stronger than CPE, it becomes brittle after long irradiations and has a tendency to crack.

Standards. Two types of multielemental standards were used. The first type was prepared by pipetting known amounts of multielemental solutions onto 5.5 cm Whatman 41 filters. The filters were air dried, pelletized and doubly sealed in polyethylene bags [15]. The second type was prepared by pipetting standard solutions directly into LPE bags containing approximately 400 mg of dry Chelex-100 resin in the ammonium form, which had been prepared using the column preparation procedure previously described. The resin was allowed to dry at room temperature under Class-100 conditions after which the bags were sealed and placed within second CPE bags. Molybdenum and uranium were in separate standards since significant amounts of ^{99}Mo are produced from uranium fission.

Irradiation and Counting Parameters. Two irradiations and five counts, after appropriate decay intervals, were used to determine the twelve elements. The samples were irradiated in the RT-3 pneumatic tube facility of the NBS Research Reactor (NBSR). In this position the thermal neutron flux is $5 \times 10^{13} n \cdot cm^{-2} s^{-1}$ and the Cu/Cd ratio is approximately 70. Radial flux variations within the rabbit are ≤ 2 percent [16]. The samples were counted with Ge(Li) and Ge(HP) detectors having active volumes of 60-90 cm^3. A Nuclear Data ND 6620 computer-based analyzer system was used for data collection and reduction.

Vanadium and manganese were determined after a 2-minute irradiation. The samples, standards, and blanks were individually packaged, and each was held rigidly in place within the rabbit with poly-foam to ensure a reproducible irradiation geometry. Vanadium was determined from a 5-minute count beginning about 2 minutes after irradiation, and manganese was determined from a 10-minute count approximately 2 hours after irradiation.

The samples were then repackaged for the long irradiation. Ten to 12 samples, standards and blanks were placed within a single rabbit, and occupied two levels. The rabbits were irradiated for 2 hours, removed from the reactor, flipped end-over-end, and reinserted in the reactor for an additional 2 hours in order to compensate for the linear neutron flux drop-off within this facility. The CPE bags were removed, and Cu was determined in the samples with a 30-minute to 2-hour count, 1-2 days after irradiation. The 511 keV γ-ray produced by the annihilation of positrons emitted by ^{64}Cu ($t_{1/2}$ = 12.7 hours) was used. An investigation of potential 511 keV γ-ray emitters (discussed below) indicated that the only significant contributor to the ^{64}Cu 511 peak ($\geq$0.1%) was ^{24}Na, which produces 511 keV γ-rays by positron annihilation following pair-production events, and occurs mainly in the Pb shielding surrounding the detector. This effect was minimized by counting the samples with an unshielded detector. The Na present in the sample was due almost entirely to the LPE bag used to contain the samples. No difference was observed between the Na levels in the seawater samples and the blanks. The ^{24}Na contribution to the 511 peak was determined by irradiating some NaCl and counting in the same geometry used for the samples. The observed ratio of 511 to

1368 keV γ-rays (0.020) was used to subtract the ^{24}Na contribution from the 511 peak of the samples.

Molybdenum and uranium,(using the ^{239}Np daughter of ^{239}U) were determined by counting the samples 4 cm from the detector, at least 48 hours after irradiation. This decay period was necessary to establish the equilibrium between ^{99}Mo and its ^{99}Tc daughter. The Mo concentration in the water must be corrected for the apparent Mo produced by ^{235}U fission. The apparent Mo/U ratio was determined from the Mo and U standards irradiated with the samples. In the RT-3 facility of the NBSR, this ratio is 2.0, or 2 μg of Mo appear to be present for every 1 μg of U in the sample. This ratio would of course be different at different facilities since the epithermal to thermal cross section for Mo activation is much greater than for ^{235}U fission.

Scandium, Cr, Fe, Co, Ni, Zn, Th, and U (using the ^{140}Ba, ^{140}La, and ^{103}Ru fission products from ^{235}U) were determined by counting the samples six weeks after irradiation for 24-48 hours directly against the detector. Since uranium is determined independently from the ^{235}U and ^{238}U isotopes, the natural isotopic abundance can be checked. The only standards used for this count were those pipetted directly on the Chelex-100 resin, since counting geometry differences between samples and standards can produce large errors when counting so close to the detector.

Nickel was determined using the 811 keV γ of ^{58}Co produced by an (n,p) reaction on ^{58}Ni. This line was not always visible due to its proximity to the 816 keV ^{140}La γ, and to the relatively high background, due in part to ^{140}La. Much better statistics for Ni could be obtained by recounting the samples about 3 months after irradiation.

Tracer Studies. The recovery and behavior of each element during the preconcentration and separation procedure was investigated using radioactive tracers. The tracers were added to 100 mL of seawater prior to pH adjustment, allowed to equilibrate, and were processed in an identical manner to the one previously described for the samples.

The eluted seawater and buffer solutions were collected in polyethylene bottles, adjusted to the same volume (height) and counted. The resin samples were transferred to similar polyethylene bottles, and nitric acid was added to strip the tracers from the resin. After volume adjustment, these samples were also counted. The three types of samples were compared against each other, and against a standard (unprocessed) spike in the same geometry.

Results and Discussion

Retention on Chelex-100. The results of the tracer studies are shown in Table 2. Vanadium, Mn, Co, Ni, Cu, Zn, and U were quantitatively retained by the resin. The reproducibility of the elements not quantitatively retained, Sc, Cr, Fe, Mo, and Th, was sufficient to allow retention corrections to be made for these elements in the samples. Additional retention studies were undertaken from distilled water, and identical results, within statistical limits, were obtained for all elements with the exception of Sc, whose retention on the resin increased to 100 percent. This increase may be due to the total absence of Cl^- ion to complex with the Sc^{+3} ion.

The small quantities of the tracers in the ammonium acetate buffer are probably due to residual column dead volume from the effluent. Chromium, Mo, and Th, however, appear to have lost significant quantities in the buffer elution. This is the first evidence of any removal of elements chelated on the resin by the buffer [6,17]. This could be due to changes in the ionic form or oxidation states of these elements. Certain elemental species can be reduced by ionic exchange resins on the column. In addition, the capability to form certain anionic species could influence this phenomenon.

Resin Characteristics. This resin was found to be extremely well suited for the described procedure. When dried in the column, the resin takes on rather unique physical characteristics. When most ion-exchange resins dry, they are crumbly and tend to crack and fall apart. The 200-400 mesh Chelex-100, when air dried in the column, shrinks to about one quarter of its hydrated size, and forms a relatively hard rod that pulls cleanly away from the walls of the polypropylene column. The resin was transferred relatively easily to the polyethylene bag, and only rarely were small pieces not directly transferred, requiring some additional manipulation.

Separation from Matrix Elements. The observed separation of the elements of interest from the alkali metals and alkaline earth metals was excellent. The concentrations observed in the processed seawater samples were identical to those in the blanks, where these elements were present within the polyethylene bags. Decontamination factors of $\geq 10^7$ for Na and $\geq 10^8$ for Cs were observed. Separation from Cl also was excellent. Again the samples and blanks appeared identical, with the Cl originating in the bags. The observed decontamination factor for Cl was $\geq 10^5$.

The separation from Br was good. At least 99.9 percent of the Br (decontamination factor $\geq 10^3$) was removed. The remaining Br (≤ 0.1 percent), however, still produced a relatively high level of background radiation, and elevated dead time, during the intermediate counts. The determination of Cu, Mo, and U, however, was not seriously affected. Attempts to further reduce the Br levels by additional water washes, and by heating with an IR lamp have not been successful.

Use of 511 keV γ-ray for Copper Determination. A number of nuclides, other than ^{64}Cu, can emit 511 keV γ-rays by positron emission, by direct emission of 511 keV γ-rays, or from positron annihilation resulting from pair-production events. Most positron emitters produced by neutron activation are insignificant, compared to ^{64}Cu, when counted 1-2 days after irradiation, due to their half-lives (either too long or too short), neutron cross sections, isotopic abundances, branching ratios, or a combination of these factors. The most common positron emitter in natural materials, other than ^{64}Cu, is ^{65}Zn. A simple comparison of nuclear parameters [18,19] indicates that for the irradiation of equal masses of Cu and Zn, the 511 keV activity of ^{64}Cu would be approximately 10,000 times greater than that of ^{65}Zn 24 hours after irradiation, and approximately 3000 times greater 48 hours after irradiation. In practice, ^{65}Zn can easily be detected by the presence of its 1115 keV γ-ray since ^{65}Zn emits approximately seventeen 1115 keV γ-rays for each 511 keV γ-ray [18,19]. Using a typical germanium detector approximately nine 1115 keV γ-rays are seen for each 511 keV γ-ray emitted by ^{65}Zn, due to the difference in detector efficiencies. The ^{65}Zn contribution to the 511 peak could easily be detected, and subtracted (if significant) using the 1115 keV peak. The presence of ^{65}Zn was not detected while counting the samples for Cu, and any possible interference was <0.05 percent for counts 48 hours after irradiation and <0.01 percent for counts 24 hours after irradiation. The other positron emitters were similarly investigated and found to be insignificant.

There are three nuclides produced by neutron activation that have half-lives long enough to be visible one day after irradiation and emit γ-rays with energies within 2 keV of 511 [19]: ^{76}As; ^{140}La, and ^{187}W. In each case the 511 keV γ-ray is a very weak line, and other γ-rays are emitted with much greater intensities. The As (which is not retained by the resin) and W γ-rays were not observed during the Cu counts, while the ^{140}La γ-rays were observed in some of the later Cu counts as ^{140}La was produced from the decay of ^{140}Ba (fission product). The ^{140}La interference for these samples was $\approx$0.01 percent, which was considered negligible.

The vast majority of the 511 keV γ-rays typically seen 1-2 days after irradiation, other than those from ^{64}Cu, result from positron annihilation following pair-production especially in the Pb shield surrounding the detector. This can be greatly reduced by counting the samples with an unshielded detector. Eliminating the shield reduces this type of 511 by greatly increasing the distance from the detector to regions where pair-production/annihilation events can occur, such as the walls of the room, floor, ceiling, etc. In addition, removing the Pb shield greatly reduces the atomic number (Z) of the stopping material. Since the probability of pair-production increases as Z^2 of the stopping material, while that for Compton scattering increases as Z [20], fewer pair-production events occur, further reducing the number of 511 keV γ-rays.

Since relatively high energy γ-rays are required for pair-production, their presence can be easily detected. One to two days after irradiation, the major producer of pair-production events is the 2754 keV γ-ray of ^{24}Na. This interference can be easily determined, as previously described, and subtracted from the samples. The observed ratio of the 511 to 1368 keV γ-rays of ^{24}Na for the detector, counting geometry and room used was 0.020, and the resulting correction for the ^{24}Na contribution to the 511 keV peak in the samples ranged from 0.1 - 1 percent.

A final check of the Cu determinations was made by counting some of the samples twice, with at least 24 hours between counts. The observed decay of the 511 peak matched the half-life of ^{64}Cu within a few percent, which can be attributed to the counting statistics.

Blanks. The concentration of the blanks is an important part of any trace element analysis. Despite the careful handling of samples, and the precautions taken, the blank levels for some elements were significant compared to the levels of trace elements in the samples analyzed, and to typical seawater (Table 1). The blank concentrations observed are listed in Table 3. These blanks represent a "total process blank" and were prepared using NBS high purity water [21]. This water was treated in a manner identical to that of the samples, including: filtration in the field, acidification, storage and chemical manipulation. There was no correction for the elemental concentrations in the water itself, since this cannot be measured for most of the elements of interest. Some elements were not normally distributed among the blanks. This would be extremely important when single (unique) samples are analyzed.

The relatively high Cr blank is due almost entirely to the LPE bag used to contain the samples. If this presents a problem, another type of polyethylene could be used, or else the samples could be carefully transferred before the Cr count. The relatively high Mn and V blank values were due primarily to the outer CPE bag which was not removed after the short irradiation, in order to minimize the possibility of contamination. The blank levels for these elements could be significantly reduced by transferring the samples to new outer bags after the short irradiation.

Trace Elements in Water - SRM 1643a. National Bureau of Standards-Standard Reference Material 1643a was used to check the analytical procedures, and to test the applicability of this procedure to a low-salinity water sample. This synthetic water standard prepared at NBS was designed to approximate a filtered and acidified fresh water sample [14]. The sample sizes used for analysis were varied from 8-50 grams. The results obtained are listed in Table 4, and agree well with the certified values. Concentrations for Sc, Th, and U are not reported since these elements were not added to this SRM. The relatively large variability observed for Fe was due partially to the counting statistics, but was also significantly affected by the variability of the blanks (especially important for the smaller samples), as shown in Table 3.

Seawater Samples. The results obtained for the replicate analysis of seawater are listed in Table 5. The previous results obtained by GFAAS, XRF, and IDMS for this material are also listed in Table 5. The concentrations of Cu, Fe, Mn, Ni, U, and Zn determined by NAA agree with the values determined by the other analytical techniques within the stated uncertainties.

The agreement between the concentrations determined by NAA and GFAAS is not only significant from an analytical view, but also from a sample stability view. The first step in the analysis of any water sample is its collection and stabilization for the particular parameters of interest. Since approximately 3 years had elapsed between the analysis by GFAAS and that by NAA, the sample had indeed been stabilized by the addition of nitric acid, at least for Cu, Fe, Mn, Ni, and Zn. This stability gives added confidence in the integrity of other natural water samples preserved in a similar manner.

The concentrations of Co, Fe, Sc, and Zn found in this water sample are essentially the same as those reported by Riley and Skirrow [1] and listed in Table 1. The slightly lower concentrations of Mo, Ni, U, and V in this sample may reflect a slight dilution of the seawater with fresh water from the Chesapeake Bay. The concentrations of Cr, Cu, and Mn are slightly elevated above the seawater values, possibly due to a localized or general source in the Bay itself. The Th concentration observed was much lower than the previously reported value for seawater [1]. Since approximately 4 years had elapsed between collection and analysis, and no long-term study of Th stability has been reported, the stability of this element is uncertain under these conditions. However, a large number of additional water samples have been collected throughout the Chesapeake Bay and processed within 1-3 months. The dissolved Th concentrations were typically ≤0.0002 ng/mL near the mouth of the Bay, and about 0.001-0.002 ng/mL near the top of the Bay.

Conclusion

The application of the Chelex-100 resin separation and preconcentration, with the direct use of the resin itself as the final sample for analysis, is an extremely useful technique. The elements demonstrated to be analytically determinable from 100 mL samples of high salinity waters are: Co, Cr, Cu, Fe, Mn, Mo, Ni, Sc, Th, U, V, and Zn. The determination of Cr, and V by this technique offers significant advantages over methods requiring aqueous final forms, in view of their poor elution reproducibility. The removal of Na, Cl, and Br allows the determination of elements with short and intermediate half-lives without radiochemistry and greatly reduces the radiation dose received by personnel. This procedure has been successfully applied in a study of more than one hundred samples collected throughout the entire length of the Chesapeake Bay. The salinity of these samples varied from that of fresh water to that of Atlantic Ocean water.

References

1. J. P. RILEY, G. SKIRROW, Chemical Oceanography, Vols. I and III, Academic Press, New York, 1975.
2. J. P. RILEY, D. TAYLOR, Anal. Chim. Acta, 40 (1968) 479.
3. E. W. DAVEY, A. E. SOPER, Chapter in Analytical Methods in Oceanography, T. R. P. Gibbs Jr., Ed., Adv. Chem. Ser., 147, 1975.
4. T. M. FLORENCE, G. E. BATLEY, Talanta, 23 (1976) 179; 24 (1977) 151.
5. C. LEE, N. B. KIM, I. C. LEE, K. S. CHUNG, Talanta, 24 (1977) 241.
6. H. M. KINGSTON, I. L. BARNES, T. J. BRADY, T. C. RAINS, M. A. CHAMP, Anal. Chem., 50 (1978) 2064.
7. H. KINGSTON, P. A. PELLA, Anal. Chem., 53 (1981) 223.
8. E. C. KUEHNER, R. ALVAREZ, P. J. PAULSEN, T. J. MURPHY, Anal. Chem., 44 (1972) 2050.
9. J. W. USELLER, NASASP-5074, Office of Technology Utilization, NASA, Washington, D.C., 1969.
10. J. R. MOODY, R. M., R. M. LINDSTROM, Anal. Chem., 49 (1977) 2264.
11. E. J. MAIENTHAL, D. A. BECKER, Natl. Bur. Stand. (U.S.), Tech Note, 926, 1976.
12. J. R. MOODY, H. L. ROOK, P. J. PAULSEN, T. C. RAINS, I. L. BARNES, M. S. EPSTEIN, Natl. Bur. Stand. (U.S.) Spec. Publ., 464, W. A. Kirchhoff, Ed., 1977.
13. W. R. KELLY, Personnel Communication 1981.
14. Natl. Bur. Stand. (U.S.), Certificate of Analysis, SRM 1643a, 1980.
15. R. R. GREENBERG, Anal. Chem., 51 (1979) 2004.
16. D. A. BECKER, P. D. LaFLEUR, J. Radioanal. Chem., 19 (1974) 149.

17. H. M. KINGSTON, "Quantitative Ultratrace Metal Analysis of High Salinity Water Utilizing Chelating Resin Separation," Interagency Energy-Environmental Research and Development Program Report, EPA/NBS, EPA-600/7-79-174 (1979).

18. C. M. LEDERER, V. S. SHIRLEY, Eds., Table of Isotopes, Seventh Ed., John Wiley and Sons, New York, 1978.

19. I. M. H. PAGDEN, G. J. PEARSON, J. M. BEWERS, J. Radioanal. Chem., 8 (1971) 127; 8 (1971) 373; 9 (1971) 101.

20. R. D. EVANS, The Atomic Nucleus, McGraw-Hill, New York, 1955.

21. T. J. MURPHY, Natl. Bur. Stand. (U.S.), Spec. Publ. 422, P. D. LaFleur, Ed. (1976).

Abstract

A procedure is described for the preconcentration of 100 mL of estuarine and seawater into a solid sample using Chelex-100 resin. This solid sample weighs less than half a gram and contains the transition metals and many other elements of interest, but is essentially free from the alkali metals, the alkaline earth metals, and the halogens. The concentrations of Co, Cr, Cu, Fe, Mn, Mo, Ni, Sc, Th, U, V, and Zn have been determined in seawater when this procedure was coupled to neutron activation analysis.

Table 1. Elemental Concentrations in Seawater.

Concentration - ng/mL[a]

Major Elements		Minor Elements	
Na	1.08×10^7	Sc	6×10^{-4}
K	3.8×10^5	V	2.5
Mg	1.3×10^6	Cr	0.3
Ca	4.1×10^5	Mn	0.2
Sr	8×10^4	Fe	2
S	9×10^5	Co	0.05
Cl	1.9×10^7	Ni	1.7
Br	6.7×10^4	Cu	0.5
		Zn	4.9
		Mo	10
		Th	0.01
		U	3.2

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[a] From ref. 1.

Table 2. Recovery and Characterization of Selected Trace Elements from Seawater

Element	Isotope	Percent Retention[a]		
		Seawater Effluent	Ammonium Acetate Buffer	Chelex-100 Resin
Co[b]	^{60}Co	0.30 ± 0.04	<0.03	99.5 ± 0.3
Cr	^{51}Cr	4.16 ± 0.26	0.90 ± 0.07	94.94 ± 0.33
Cu[b]	^{64}Cu	0.026 ± 0.002	<0.002	99.97 ± 0.03
Fe[b]	^{59}Fe	6.3 ± 1.9	0.41 ± 0.01	93.1 ± 2.2
Mn[b]	^{54}Mn	<0.05	<0.02	99.99 ± 0.11
Mo	^{99}Mo	1.00 ± 0.17	0.62 ± 0.03	98.38 ± 0.19
Ni[b]	^{65}Ni	0.09 ± 0.01	<0.004	99.91 ± 0.08
Sc	^{46}Sc	14.58 ± 0.18	0.59 ± 0.05	84.84 ± 0.22
Th	^{230}Th	12.74 ± 0.42	4.44 ± 0.50	82.83 ± 0.34
U	^{235}U	<0.2	<0.1	99.8 ± 0.2
V	^{48}V	2.36 ± 0.34	0.04 ± 0.03	97.58 ± 0.34
Zn[b]	^{65}Zn	0.04 ± 0.01	<0.02	99.97 ± 0.03

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[a] Uncertainties are at the 1s level

[b] Reported previously in ref. 6

Table 3. Blank Concentrations — ng/g[a]

Co	0.012 ± 0.009	Ni	<0.2
Cr	1.55 ± 0.10	Sc	0.00012 ± 0.00004
Cu	0.17 ± 0.04	Th	0.0005 ± 0.0002
Fe	1.3 ± 0.6	U	<0.01
Mn[b]	0.17 ± 0.18	V[b]	0.12 ± 0.03
Mo	<0.01	Zn	0.6 ± 0.2

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[a] Uncertainties are 1s for at least 5 blanks

[b] Includes outer bag

Table 4. Trace Elements in Water — SRM 1643a

	Concentration — ng/g	
Element	This Work[a]	Certified[b]
Co	19 ± 1	19 ± 2
Cr	16 ± 2	17 ± 2
Cu	19.1 ± 0.6	18 ± 2
Fe	88 ± 16	88 ± 4
Mn	30.9 ± 0.6	31 ± 2
Mo	97 ± 6	95 ± 6
Ni	56 ± 8	55 ± 3
V	52 ± 1	53 ± 3
Zn	68 ± 5	72 ± 4

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[a] Uncertainties are 2s

[b] Uncertainties are 95% confidence limit

Table 5. Trace Elements in One Seawater Sample

	Concentration – ng/mL[a]			
Element	NAA[b]	GFAAS[c]	XRF[d]	IDMS[e]
Co	0.043 ± 0.005	<0.1		
Cr	3.3 ± 0.2			
Cu	2.01 ± 0.05	2.0 ± 0.1	2.0 ± 0.2	
Fe	2.1 ± 0.3	2.1 ± 0.5		
Mn	1.89 ± 0.03	2.0 ± 0.1	2.0 ± 0.1	
Mo	5.3 ± 0.1			
Ni	1.2 ± 0.2	1.2 ± 0.1	1.3 ± 0.2	
Sc	0.00096 ± 0.00004			
Th	≤0.0002			
U	1.90 ± 0.04			1.91 ± 0.01
V	0.45 ± 0.01			
Zn	4.8 ± 0.2	4.8 ± 0.3	4.5 ± 0.4	

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[a] All uncertainties are at the 1s level

[b] This work

[c] From ref. 6

[d] From ref. 7

[e] From ref. 13

APPENDIX 3

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Separation of Eight Transition Elements from Alkali and Alkaline Earth Elements in Estuarine and Seawater with Chelating Resin and Their Determination by Graphite Furnace Atomic Absorption Spectrometry

H. M. Kingston,* I. L. Barnes, T. J. Brady, and T. C. Rains

National Measurement Laboratory, Center for Analytical Chemistry, Inorganic Analytical Research Division, National Bureau of Standards, Washington, D.C. 20234

M. A. Champ

The American University, Washington, D.C. 20016

A method is described for determining Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn in seawater using Chelex 100 resin and graphite furnace atomic absorption spectrometry. The pH of the seawater is adjusted to 5.0 to 5.5 and then passed through a Chelex 100 resin column. Alkali and alkaline earth metals are eluted from the resin with ammonium acetate and then the trace elements are eluted with two 5-mL aliquots of 2.5 M HNO_3. The difficulties previously encountered with resin swelling and contracting have been overcome. By careful selection of the instrumental conditions, it is possible to determine subnanogram levels of these trace elements by graphite furnace atomic absorption spectrometry. The proposed method has been shown to separate quantitatively the elements desired from the alkali and alkaline earth metals and has been applied in the analysis of trace elements in estuarine water from the Chesapeake Bay and seawater from the Gulf of Alaska.

The literature of marine water analysis reflects the considerable difficulty in establishing an accurate and precise method of analysis for trace metals. A seawater matrix defies a simplified approach. For example, specific sampling techniques, container contamination, suspended particulate matter, and analytical techniques have to be considered. It is beyond the scope of this paper to discuss all of these parameters; however, the solving of the analytical problem is of little value unless a representative sample can be obtained, free of contamination and properly stored until analysis.

In recent years, methods have been developed to determine trace elements in seawater by X-ray fluorescence (*1*), neutron activation (*2*, *3*), spectrophotometry (*4*), anodic stripping voltammetry (*5*), and atomic absorption spectrometry (*6–8*). However, each of these analytical techniques requires a preliminary separation. Fabricand et al. (*9*) reported the direct determination of Cu, Fe, Mn, Ni, and Zn in seawater by atomic absorption spectrometry (AAS) using an air–acetylene flame, but other workers have reported difficulties using their technique because of light scattering and burner clogging.

Except for neutron activation analysis and anodic stripping voltammetry, no analytical techniques are currently available for the direct determination of trace elements in seawater at concentrations below 5 $\mu g\ L^{-1}$. Usually it is necessary to preconcentrate the trace elements from a large volume and separate the transition elements from the alkali and alkaline earth elements. In such sample preparations, the efficiency of concentration, completeness of separation, and total analytical blank become critical to the final instrumental method (*10*).

Preconcentration techniques which have been used are coprecipitation (*11*), chelation and extraction (*12*), and chelating ion-exchange resin (*10*, *13*). Most of these isolation methods require large volumes of chemicals which can lead to high blanks unless the reagents have been carefully purified.

Of the presently used preconcentration techniques, Chelex 100 chelating resin has been shown to be efficient and yields low analytical blanks (*14*). Applications of Chelex 100 resin for trace metal preconcentration from seawater have been reviewed by Riley and Skirrow (*10*). Chelex 100 is a strong chelator and removes metal ions from most known naturally occuring chelators in seawater (*14–16*). The resin will not, however, remove metals held in organic and inorganic colloids which can be present even after ultrafiltration. Precautions

Table I. Instrumental Parameters

		P & E 603		HGA-2100			
element	wavelength, nm	SBW, nm	scale expansion	drying, *T*-sec[c]	charring *T*-sec	atomization *T*-sec	gas
Cd	228.8	0.7	1	100-30	200-20	2100-7	Ar[a]
Co	240.7	0.2	2	100-30	500-30	2700-7	Ar[a]
Cu	324.7	0.7	1	100-40	700-30	2500-6	Ar[a]
Fe	248.3	0.2	2	100-30	600-30	2700-7	Ar[a]
Mn	279.5	0.7	2	100-30	300-30	2700-7	Ar[a]
Ni	232.0	0.7	5	100-30	1000-30	2700-6	Ar[a]
Pb	283.3	0.7	3	100-40	400-30	2200-7	Ar[b]
Zn	213.9	0.7	0.5	100-30	500-20	2000-7	Ar[b]

[a] Interrupt mode. [b] Normal mode. [c] Note: *T* = temperature.

must be taken to destroy such colloids prior to collection of the ions by the resin. Florence and Batley have destroyed interfering organic colloids by the addition of 0.16 M nitric acid and heat and also by using ultraviolet irradiation of the sample prior to collection by the resin (*15, 16*). While excellent recovery and low analytical blanks are achieved, a relatively high concentration of Na, K, Ca, and Mg are retained with the trace metals. The concentration of these interfering alkali and alkaline earth salts in the final sample are in milligram quantities, as compared to the microgram and submicrogram quantities of concentrated trace metals. The alkali and alkaline earth ions occupy the resin sites not occupied by the transition metals and are co-eluted with the metals when using acids (*13*).

The complete separation of the alkali and alkaline earth metals from the trace metals in seawater has not been previously accomplished using Chelex 100, which has restricted its use. While the salts remaining after preconcentration do not interfere with instrumental techniques such as flame atomic absorption (*10*) or polarography (*15–17*), they do inhibit instrumental techniques which are more susceptible to matrix interelement effects such as flameless atomic absorption (*18*), neutron activation analysis (*19*), optical emission spectrometry using inductively coupled plasma or electrode plasma (dc arc) (*20*), and spark source mass spectrometry (21).

With the development of the graphite furnace for AAS, it is now possible to determine 10^{-9} to 10^{-12} g of many of the trace elements in seawater. However, the high salt content (35 g/kg) in marine water makes it difficult to effectively volatilize the matrix without loss of analyte. The major component in seawater is sodium chloride which has a relatively high volatilization temperature. Also, the trace metals in seawater are present as chlorides, which have a lower volatilization temperature. Therefore, it is difficult to volatilize the sodium chloride during the ashing step without losses of the analyte. Calcium and magnesium chloride are also present in seawater in large quantities and a temperature greater than 2000 °C is required to volatilize these elements. Thus, even if the sodium chloride is removed during the ashing step using matrix modification (*22*), residual calcium and magnesium chlorides remain to interfere with the analyte during atomization.

The research presented here describes a technique for the separation and preconcentration of Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn from Na, K, Ca, and Mg in seawater using a Chelex 100 resin column and the subsequent determination of these trace elements by graphite furnace atomic absorption spectrometry (GFAAS).

EXPERIMENTAL

Reagents. High purity water, nitric and glacial acetic acids were prepared using subboiling distillation at the National Bureau of Standards (NBS) (*23*). All reagents used in the separation process were prepared and stored in clean FEP Teflon bottles unless otherwise stated.

Ammonium hydroxide was prepared by bubbling filtered ammonia gas through high purity water until room temperature saturation was achieved.

A 1.0 M ammonium acetate solution was prepared by mixing 60 g of purified glacial acetic acid and 62 g of saturated NH_4OH and diluting to 1 L in a polypropylene volumetric flask. The acidity was adjusted to pH 5.0 by dropwise addition of HNO_3 and/or NH_4OH. All reagent and sample preparations were done in a class 100 clean air laboratory (*24*).

Chelex 100 chelating resin, 200–400 mesh size, was purchased from Bio-Rad Laboratories.

The radioactive tracers ^{59}Fe, ^{54}Mn, and ^{65}Zn in 0.5 N HCl were purified reagents obtained from the Chemical and Radioisotope Division of ICN. The ^{60}Co, and the short lived isotopes, ^{64}Cu and ^{65}Ni, were made by the Neutron Activation Analysis Group at NBS from "five-9's" pure metals and dissolved in nitric acid. The ^{109}Cd and ^{210}Pb were obtained by the Activation Analysis Group from other sources and analyzed using pulse height analysis for radiochemical purity before use.

All standard stock solutions for AAS were prepared from high purity metals or salts in subboiling distilled NBS acids as described by Dean and Rains (*25*). Working solutions were prepared as needed.

Counting Apparatus. The γ-ray counting of the elemental tracers was done utilizing a 7.6 cm × 7.6 cm NaI(Tl) crystal and associated electronics.

Seawater. The seawater was obtained during high tide at the Virginia Institute of Marine Science (VIMS), Gloucester Point, Va., on the Chesapeake Bay. The sample was collected with a submersible pump and plastic tubing permanently submerged approximately 100 m offshore from the Institute. The seawater was pumped directly into a conventional polyethylene drum which had been cleaned first with hydrochloric and then with nitric acid and purified water prior to use (*26*). After filtration through a 0.45-μm millipore filter using an all polypropylene filter apparatus, the seawater was collected in a polyethylene carboy and acidified (to 0.6 M in HNO_3) with high purity HNO_3 to prevent bacterial growth, to stabilize the trace element concentrations (*27, 28*), and to strip any trace elements bound by colloidal particles (*15, 16*).

AAS Apparatus. The instrumental system used in this study consists of a Perkin-Elmer Model 603 atomic absorption spectrometer with HGA-2100 graphite furnace (GFAAS). The 25-μL aliquot of sample was introduced into the furnace with the AS-1 autosampler. The instrumental parameters are given in Table I.

Column Separation Apparatus. The Isolab QS-Q polypropylene column with porous polyethylene resin support was used for 100-mL and 1-L sample volumes. Although the same column was used for both sample volumes, the amount of resin and reservoir systems were entirely different. For the 100-mL sample, the QS-S 25-mL conventional polyethylene extension funnel was attached to the column to act as a reservoir for the sample.

For a 1-L sample the reservoir was a 1-L Teflon (FEP) bottle inverted and modified with a machined Teflon (TFE) closure insert containing a microbore venting tube and outlet tube. The outlet was connected to a valve (TFE) by 1.59-mm ($^1/_{16}$ in.) i.d. Teflon (FEP) tubing connector and linked to the reservoir with a specially machined mount (TFE) which sealed the column into the closed system. The mount contained a vent (sealed with nylon

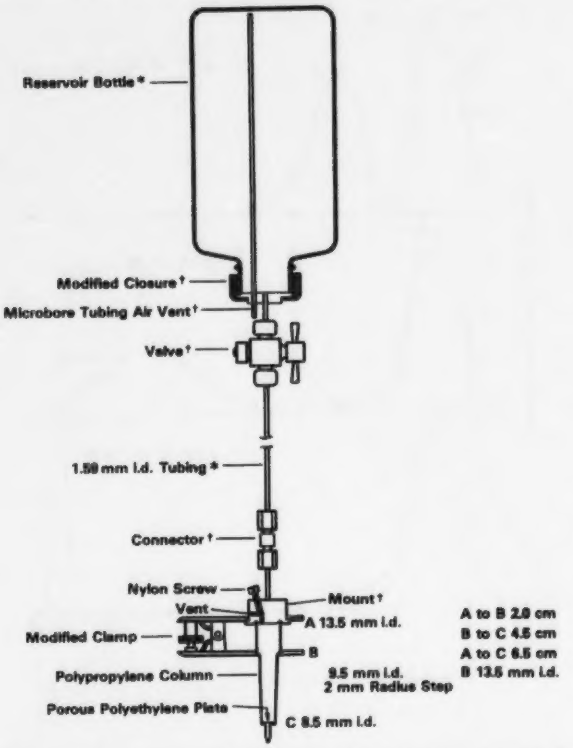

Figure 1. Apparatus used for holding and delivering large volumes of seawater at a controlled rate to Chelex 100 resin. The apparatus (excluding the column and clamp) was fabricated from Teflon FEP (*) or Teflon TFE (†) which has desirable nonwetting and noncontaminating properties

screw, allowing the removal of air from the system) as well as an inlet and was tightly clamped to the column using the lip on the column at point B (See Figure 1). The clamp (a modified glass joint clamp) and mount provided a seal which allowed the reservoir to be raised above the column to obtain enough pressure to control the flow rate using the pressure of the raised reservoir and the valve (Figure 1).

Column Preparation and Purification Procedure. The column preparation procedure consisted of precleaning the columns in 1:4 HCl and then in 1:4 HNO_3 for one week in each bath and then rinsing the columns with water after each acid wash. The column was loaded with a slurry of Chelex 100 resin, 200–400 mesh size (sodium form). For 100-mL seawater samples, 3.2 to 3.4 mL of resin was used which covered the lower barrel of the column from point B to point C in Figure 1. For 1-L samples, 5.8 to 5.9 mL of resin was used which filled the column from point A to point C in Figure 1. The resin was washed with 15 to 20 mL of 2.5 M HNO_3 (for the small and large resin volumes, respectively), in 5-mL portions to elute any trace metal contamination present in the resin. Then two 5-mL volumes of water were used to rinse the resin of excess acid. To transform the resin to the NH_4^+ form, 10 to 15 mL of 2.0 M NH_4OH was added in 5-mL volumes. After checking the pH of the effluent to ensure basicity, the column was then rinsed with 10 to 15 mL of water to remove the excess NH_4OH.

Column Preconcentration and Separation Procedure. For the 100-mL seawater sample, 101.8 ± 0.2 g was weighed directly into a clean 250-mL Teflon (FEP) beaker and the pH adjusted to 5.0 to 5.5 with the dropwise addition of NH_4OH. If a spike (natural or radiochemical) was to be added, it was added prior to the adjustment of the pH to equilibrate the ions in the acid media; the solution was allowed to equilibrate for a minimum of 1 h after the addition of any spike. Then 0.5 mL of 8 M ammonium acetate was added to aid in buffering the system. Any necessary agitation of the solution was done with a Teflon stirring rod. A small amount of the seawater was added to the reservoir and column to allow the resin to undergo its natural shrinkage as it changes ionic form and pH. This shrinkage results in a resin volume of approximately one half of its original volume. After the completion of this transformation was observed (2 to 3 min), the remaining seawater was added to the reservoir as needed to keep it filled; the flow rate was approximately 0.8 mL/min. To selectively elute Na, K, Ca, and Mg, and replace them with NH_4^+, 40 mL of 1.0 M ammonium acetate was added to the column in 10-mL aliquots. At the completion of the ammonium acetate addition, 10 mL of water was added to remove residual ammonium acetate. The transition metals were then eluted using 7 mL of 2.5 M HNO_3 and collected into clean preweighed 10-mL conventional polyethylene bottles. The bottles were capped with clean polyethylene lined caps and reweighed to determine the weight of the effluent accurately.

The procedure for the 1-L samples was the same as the 100-mL samples with minor alterations due to the apparatus (see above). The sample (1018.0 ± 0.5 g) was weighed into a 1-L Teflon (FEP) bottle and the pH adjusted in the same manner as previously described. The bottle became the reservoir and was fitted with a modified closure (see Figure 1). The bottle was inverted and the air purged from the system by means of the vent on the column mount. The flow rate was adjusted using the valve and the height of the reservoir. The flow rate was kept to less than 0.2 mL/min until the shrinkage of the resin was complete. Then the flow rate was increased to 1.0 mL/min and left overnight to flow through the column. After passing the sample through the column, the valve and tubing were removed at the connector above the column mount and replaced with a smaller reservoir containing 70 mL of 1.0 M ammonium acetate. The flow rate was adjusted to 0.5 mL/min until the reagent was exhausted. The resin was then washed with 10 mL of water. The transition metals were eluted with two 5-mL portions of 2.5 M HNO_3 into preweighed polyethylene bottles as previously described.

RESULTS AND DISCUSSION

Effect of Direct Injection of Seawater into Electrothermal Device. From the detection limits published in the literature for GFAAS, it could be assumed that several of the heavy metals in seawater could be determined by direct injection of the sample into the electrothermal device. However, in reality this has not been proved to be true unless the samples are taken from heavily polluted areas. A sample from the Chesapeake Bay was analyzed for Cd, Co, Cu, Mn, Ni, Pb, and Zn by direct injection into the graphite furnace by AAS. Only lead and nickel produced absorption signals of any analytical value. The other elements could not be detected. This is due in part to the highly depressing effect of the matrix on the analyte signal which can vary by a factor of 2 to 10 depending upon the analyte. Also, when the sample is evaporated, a small amount of solution may be trapped in the salt crystal lattice which could result in losses due to splattering during the atomization cycle.

The absorbances obtained for lead and nickel were very erratic due to the smoke produced during atomization. Ediger et al. (*22*) used matrix modification with ammonium nitrate to assist in the removal of sodium chloride; however, the method of standard addition was necessary to correct for interferences. In applying their method of matrix modification to the Chesapeake Bay sample, Cd, Co, Cu, Fe, Mn, and Zn were still not detected.

Separation of Calcium and Magnesium from Analytes on Chelex 100. To effect a separation of calcium and magnesium from the trace elements on the Chelex 100 resin column, it is necessary to choose a separating agent that can be purified to produce a low analytical blank. Also, the separating agent should not produce any adverse effects on the analytes in the GFAAS analysis. The ammonium ion reacts similarly to the alkali elements, and ammonium nitrate or acetate can be produced from high purity reagents.

While both ammonium nitrate and ammonium acetate remove sodium and potassium at identical rates, ammonium nitrate produced tailing of the calcium and magnesium which

Table II. Concentration of Alkali and Alkaline Earth Metals in Seawater before and after Separation on Chelex 100 Resin Column

	µg/mL			
sample	Na	K	Ca	Mg
original	6200	267	283	742
	after separation[a]			
wash[b]				
H_2O	320	10	350	63.
NH_4NO_3	0.3	0.7	83	1.3
NH_4COOCH_3	1.0	2.0	0.25	<0.05

[a] 100 mL of seawater preconcentrate into 7 mL of 2.5 M HNO_3. [b] Column washed with 50 mL of a given eluent.

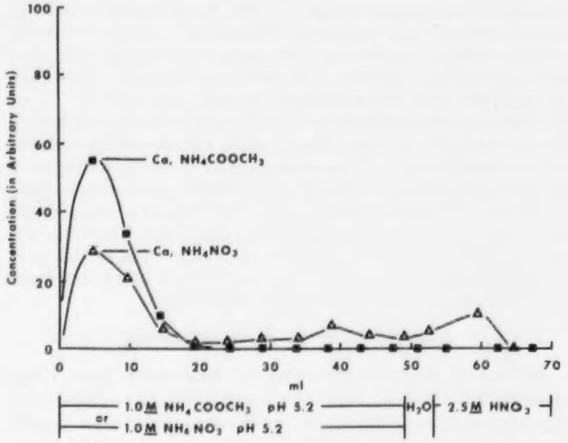

Figure 2. Comparison of ammonium acetate vs. ammonium nitrate for the separation of calcium from a Chelex 100 resin column which has previously chelated 100 mL of seawater

left appreciable quantities of these alkaline earths in the final HNO_3 effluent (Figure 2) (Table II). However, ammonium acetate eluted calcium and magnesium from the column with tailing of only 1 to 2 bed volumes (Figure 2). Manganese, which has the smallest selectivity coefficient of the transition metals of interest, was not eluted at pH 5.0 by ammonium acetate or ammonium nitrate. A relatively high concentration of ammonium acetate in the 2.5 M HNO_3 effluent produced a suppression of several of the analytes by GFAAS; however, the problem was alleviated by washing with 5 to 10 mL of water prior to the stripping of the column with the 2.5 M HNO_3 (Figure 2).

There is a contribution to the removal of calcium and magnesium from the resin by the acetate anion which does not appear with the nitrate ion. Sodium and potassium are replaced by the ammonium ion, but this cation is only partially responsible for the complete separation of chelated calcium and magnesium using ammonium acetate.

Effect of pH on the Separation. A study of the pH of the separating agent (1 M ammonium acetate) showed that a minimum pH of 5.0 was required to retain the transition metal ions on the Chelex 100 resin while removing the alkali and alkaline earth ions. Below pH 5.0, it was found that the transition metals were eluted by the 1 M ammonium acetate. From pH 5.0 to 5.5, the transition metals Cd, Co, Cn, Fe, Mn, Ni, Pb, and Zn were retained by the resin while the Na, K, Ca, and Mg were quantitately eluted (see Figure 3).

The chelating efficiency of Chelex 100 increases for the transition metals from pH 4 to 5 and reaches an optimum at approximately pH 5.0. For most of the transition elements, this optimum efficiency remains for an increase of several pH units. However, the chelating efficiency of Chelex 100 for Co and Cu has been shown to decrease above pH 6.0 (*29–32*).

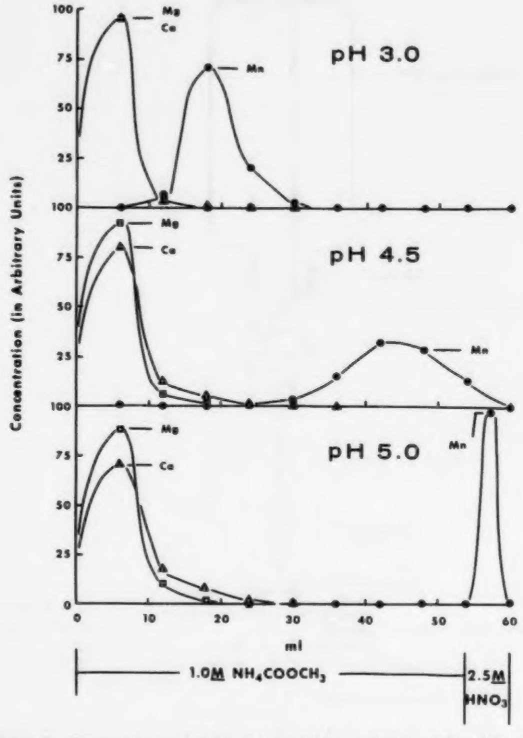

Figure 3. Comparison of ammonium acetate elution of Ca, Mg, and Mn in the pH range of 3.0 to 5.0. The graph depicts percent of the total column content of an element eluted with volume

The chelation efficiency of Chelex 100 for Ca and Mg has been reported to be similar to those of the transition metals increasing with pH to a maximum at pH 5 in low ionic strength solutions (*30*, *33*). However, in high ionic strength solutions of sodium chloride, there exists a minimum in the chelation of Chelex 100 for both Ca and Mg from pH 5.0 to 5.8. Above pH 5.8 the chelating efficiency for Ca and Mg increases sharply (*33*).

From our experimental results and the literature, a working range of pH 5.0 to 5.5 was established for both the preconcentration of the transition elements from the seawater and the elution of the alkali and alkaline earth elements from the resin using the ammonium acetate.

Separation Parameters for Both 100-mL and 1-L Seawater Samples. The separation parameters, as described in the Procedure section, are represented graphically for a 100-mL sea water sample in Figure 4, and for a 1-L sample in Figure 5. The difference between the two systems is approximately double the amount of resin for the 1-L sample. The larger amount of resin was found to be necessary for quantitative retention of this larger volume, but is still rather small considering a 10-fold increase in the total ionic content of the larger sample. An increased volume of ammonium acetate was required for the removal of the greater quantity of salts occupying more residual sites. Also, a larger volume of water is required to wash the residual ammonium acetate from the column prior to transition metal elution with nitric acid. The elimination of ammonium acetate was found to be necessary to prevent both buffering of the acid wash and a suppression of the GFAAS signal caused by the acetate in the subsequent analysis. The acid fraction did not undergo tailing

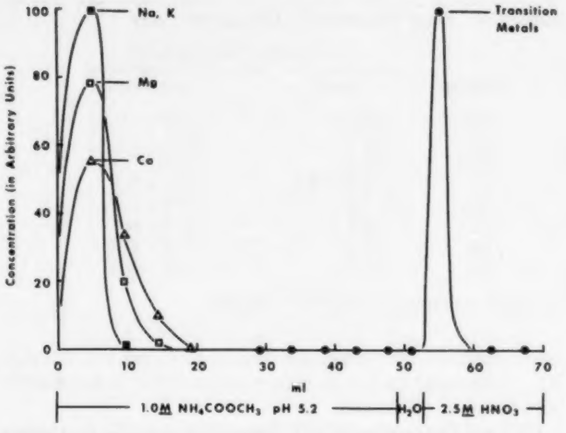

Figure 4. Represents the separation obtained using 1.0 M ammonium acetate at pH 5.0 to 5.5 for the transition metals from Na, K, Ca, and Mg chelated in a column of Chelex 100 from a 100-mL seawater sample

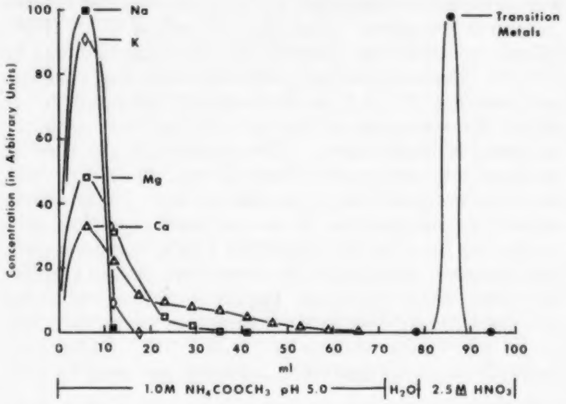

Figure 5. Represents the separation obtained using 1.0 M ammonium acetate at pH 5.0 to 5.5 for the transition metals from Na, K, Ca, and Mg chelated on a column of Chelex 100 from a 1-L seawater sample

from the transition metals as seen by atomic absorption or by radio tracer studies. The Chelex 100 resin in the presence of 2.5 M HNO_3 does not chelate the transition metals and they are eluted simultaneously into a single small volume of acid.

Chelex 100 resin is a dynamic resin, and in the ammonium form at a pH of 7 to 14, the resin shrinks to approximately $^1/_2$ of its original volume when subjected to the seawater sample at pH 5.0 to 5.5. The particle size and subsequent flow rate were also reduced and the use of the column apparatus for 1-L samples became necessary to increase the pressure of the sample to obtain a realistic flow rate for both the sample and ammonium acetate. The flow rate of 1 mL/min was attained by adjusting the Teflon valve and reservoir height simultaneously to control the pressure. The residual volume which would retain any sample in the entire apparatus was estimated at less than 0.10 mL. The use of all Teflon components in contact with the sample affords the nonwetting characteristics and noncontaminating nature of this fluorocarbon which can be scrupulously cleaned in acid (*26*). Another important benefit of this apparatus is that during the preconcentration onto the Chelex 100, the sample and column are protected from contamination from the environment; the only entrance into the system is a microbore tube which can be fitted with a filter to exclude particulate contamination. These characteristics make the column apparatus very attractive for field or shipboard use to prevent contamination.

Radiochemical Study. Radiochemical tracers were used to gain specific information about the behavior of each ion during preconcentration and separation using the Chelex 100. The tracers were added to the seawater as one radioisotope per sample prior to the pH adjustment. The column procedure was identical in all respects to the preparation of the analytical samples previously described. However, all effluent from the column was collected, including the seawater. The seawater, ammonium acetate buffer, acid effluent, and column resin were collected in polyethylene bottles. The 1-L samples were collected in 250-mL bottles and the 100-mL samples were collected in 125-mL bottles. Distilled water was added to the bottles prior to measurement to make all liquid levels the same to give constant counting geometry.

The samples were counted for 10-min periods for γ radiation only (Table III). The counting statistics for each element were optimized by energy discrimination. The concentration of tracers used gave from 10^6–10^7 counts in a 10-min period while background was kept to 10^2–10^3 counts during the same period. The statistical error was obtained using the following equation (*34, 35*):

$$Q_c = 100 \times \frac{k}{N_s - N_b} \sqrt{N_s + N_b}$$

where Q_c = percent experimental error corrected for background, k = number of standard deviations, N = cpm = counts per minute or period unit time, s = sample including background, and b = background.

This technique enabled the use of ^{64}Cu and ^{65}Ni short-lived isotopes as well as ^{59}Fe and ^{54}Mn intermediately-lived isotopes since counting of all fractions could be completed in 40 min. The error caused by the decay of these isotopes over the course of the experiment was eliminated; nickel which has a half life of only 2.6 h, decayed beyond usefulness over the 1-day period of the 1-L experiment.

The counting technique was checked for total recovery using ^{65}Zn. The tracer was added to 250 mL of the seawater sample and counted prior to manipulation. This volume was then added to 750 mL of seawater and treated as a 1-L ^{65}Zn spiked seawater sample. The final acid volume was then counted at the end of the separation as previously described. The total quantity obtained agreed for both the acid fraction and total recovery, 99.99 ± 0.12 and 100.1 ± 0.12, respectively. Thus, the counting of all effluent fractions and the column itself allows the specific identification of all losses, as well as the total recovery of the element of interest in the acid fraction.

The ammonium acetate separation did not remove a detectable amount of any trace metal with the possible exception of Fe which could have been in the residual volume from the seawater effluent. Thus, the separation does not affect the maximum efficiency of the concentration alone, and the Na, K, Ca, and Mg can be eliminated with the same efficiency as the traditional concentration alone.

The majority of any minute losses Pb 1.4%, Co 0.3%, and Fe 6.3% is due to incomplete removal of the transition metal ions from the seawater. The chelation efficiency of both ^{60}Co and ^{59}Fe was studied by Callahan et al. (*32*). They found that the two oxidation states of cobalt and iron reacted similarly and that 100% retention of cobalt and iron could only be achieved by reduction of Co(III) to Co(II) and Fe(III) to Fe(II) using sodium dithionite ($Na_2S_2O_4$) at pH 5.0 to 5.3. In natural seawater the approximate concentration of Co(II) was found to be 96% of the total cobalt. They obtained 96 to 99% retention for cobalt and 95% for iron without any attempt to reduce the trivalent ions, which is in agreement with our findings.

The radiochemical tracer experiments for Cd, Cu, Fe, Ni, and Zn were repeated several times and all values fell within the calculated error limits with the exception of those for iron.

Table III. Recovery and Characterization of Selected Transition Elements in Seawater Using Chelex 100

	sample, 100 mL[a]				sample, 1 L[a]			
	loss, %			recovery, %	loss, %			recovery, %
element	seawater effluent	1.0 M NH_4COOCH_3 effluent	column and resin	2.5 M HNO_3 effluent	seawater effluent	1.0 M NH_4COOCH_3 effluent	column and resin	2.5 M HNO_3 effluent
^{109}Cd	<0.06	<0.06	<0.06	99.99 ± 0.071	<0.02	<0.06	<0.012	99.99 ± 0.063
^{65}Zn	0.039 ± 0.007	<0.02	<0.02	99.96 ± 0.097	<0.01	<0.03	<0.04	99.99 ± 0.12
^{54}Mn	<0.048	<0.02	<0.006	99.99 ± 0.11	...	...	...	...
^{65}Ni	0.09 ± 0.005	<0.004	<0.004	99.91 ± 0.083	...	...	...	...
^{64}Cu	0.03 ± 0.001	<0.002	<0.02	99.97 ± 0.030	0.17 ± 0.006	<0.007	0.01 ± 0.003	99.82 ± 0.069
^{210}Pb	1.4 ± 0.10	<0.01	0.2 ± 0.13	98.4 ± 0.48	2.15 ± 0.14	<0.06	0.12 ± 0.08	97.7 ± 0.39
^{60}Co	0.3 ± 0.04	<0.03	0.17 ± 0.03	99.5 ± 0.3	1.7 ± 0.05	0.03 ± 0.01	0.9 ± 0.02	97.3 ± 0.2
^{59}Fe[b]	6.3 ± 1.9	0.41 ± 0.01	0.21 ± 0.01	93.1 ± 2.2	6.2 ± 1.9	0.90 ± 0.3	0.31 ± 0.01	92.6 ± 2.2

[a] The uncertenty is based on 1 σ values calculated as described in the text. [b] The uncertainty was increased to show additional uncertainty found in replicate experiments.

Table IV. Trace Elements in Chesapeake Bay

	concentration, ng/mL[a]	
element	blank	seawater
Cd	<0.01	0.05 ± 0.01
Co	<0.1	<0.1
Cu	<0.1	2.0 ± 0.1
Fe	0.2 ± 0.1	2.1 ± 0.5
Mn	<0.1	2.0 ± 0.1
Ni	<0.1	1.2 ± 0.1
Pb	<0.1	0.3 ± 0.2
Zn	<0.05	4.8 ± 0.3

[a] Replicate analysis of four samples.

Iron exhibited a 2% variation around the average value (Table III). This could be due to altered ratios of Fe(II) and Fe(III) between samples tested.

GFAAS Determination of Trace Elements in Seawater from the Chesapeake Bay. The reliability of the proposed separation and preconcentration method was tested by making replicate analyses on a sample of seawater. These samples were processed as described in the Separation and Preconcentration Procedure. Then the 8–10 mL of 2.5 N HNO_3 effluent collected was analyzed for the trace elements by GFAAS. The instrumental conditions for drying, charring, and atomizing (Table I) for each analyte were optimized to obtain the maximum sensitivity and precision with the minimum of interferences. The samples (25 μL) were introduced into the graphite furnace with the AS-1 which improved the precision of the analysis with the minimum amount of contamination. It was necessary to preclean each sample cup from the AS-1 with 20% HNO_3 to remove trace contaminants. Pyrolytic and nonpyrolytic coated graphite tubes were used in this study. The life of the pyrolytic coated tube was extended by a factor of three over the nonpyrolytic coated tube in the presence of 2.5 M HNO_3. Background correction with the deuterium arc lamp was used for each analyte.

For each analysis the hollow cathode lamp was turned on and allowed to stabilize (15 to 60 min). Working standard solutions of each analyte were prepared in 2.5 M HNO_3, and then a three to five point calibration curve was established using the optimum instrumental conditions. After the calibration curve was established, the unknowns were determined using a sample bracketing technique. As a check for chemical interferences, each sample was tested by the single standard addition method (*36*) and no chemical interferences were encountered. The results are given in Table IV. Cobalt was not detected using a 100-mL sample. To obtain an analytical value for cobalt in the Chesapeake Bay Water, a 1-L sample would be required to be separated and preconcentrated. Some difficulty was encountered in the GFAAS determination of iron. Iron is known to form carbides in the graphite furnace which produce erratic results. Also, a high reagent blank was obtained (see Table IV) whereas the reagent blanks for the other elements were below our detection limits. The lead values are close to the detection limit using a 100-mL sample. With a 0.5- to 1-L sample, the precision of the lead analysis could be improved.

Recovery of Trace Elements Added to Chesapeake Bay Seawater. Since there are no samples of seawater with accurate analytical values for the trace elements under study, the accuracy of the GFAAS technique was checked by adding 0.5 to 2.0 ng/mL of the trace elements to six samples of seawater and processed as previously described. Recoveries of 90 to 117% were obtained (Table V). The high recovery value for zinc was due to the low concentration added to the samples. Since zinc is so sensitive by GFAAS, a 1- to 10-fold dilution of the 2.5 M HNO_3 effluent had to be made. Since

Table V. Recovery of Trace Elements Added to Samples of Seawater by GFAAS

	concentration, ng/mL[a]			
element	present	added	found	av. recovery, %
Cd	0.05	0.5	0.54 ± 0.02	98
Co	<0.1	1.0	1.07 ± 0.02	107
Cu	2.0	1.0	2.9 ± 0.07	97
Fe	2.1	2.0	3.7 ± 0.4	90
Mn	2.4	2.0	4.2 ± 0.04	95
Ni	1.2	2.0	3.2 ± 0.1	100
Pb	0.3	1.0	1.4 ± 0.07	108
Zn	4.8	0.5	6.2 ± 0.09	117

[a] Replicate analysis of six samples.

a dilution was required for GFAAS, the original spikes added to the seawater were too low to obtain accurate recoveries. The recoveries of the other trace elements are consistent with the known reproducibility of the GFAAS at these concentration levels.

Application of the Technique to Alaskan Seawater Samples. In addition to the one homogeneous Chesapeake Bay water sample, other seawater samples were also analyzed for Cd, Mn, Ni, and Pb. These samples were obtained from the Gulf of Alaska and ranged in depth from surface to 1500 m. These samples were treated in the same manner and no alteration in the separation technique was necessary. The trace metal concentrations from Alaskan seawater were found to be generally lower in concentration over those of the Chesapeake Bay. The values for Pb and Mn were found to be consistently 1 to 2 orders of magnitude below those reported here for these same elemental concentrations in the Chesapeake Bay.

CONCLUSION

The application of Chelex 100 resin and GFAAS used in this investigation has been shown to provide a new way of determining Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn in seawater. Chelex 100 resin is known to be an efficient means of separating many of the trace elements from the alkali metals; however, by using an ammonium acetate wash, calcium and magnesium are also removed. Calcium and magnesium severely suppress many analytes in GFAAS and, with their removal, the detection limits of many trace elements by GFAAS can be extended to subnanogram per milliliter. In our radiotracer study, the recovery of Cd, Cu, Mn, Ni, and Zn was greater than 99.9% while the recovery of Co, Pb, and Fe was 99.5, 98.4, and 93.1%, respectively. The precision of the technique was limited by the GFAAS measurements which varied with the element and concentration present. Not only has the proposed technique been applied to seawater from the Chesapeake Bay but the method was applied to the determination of Cd, Mn, Ni, and Pb at the ng/mL level in seawater from the Gulf of Alaska.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) D. E. Leyden, T. A. Patterson, and J. J. Alberts, *Anal. Chem.*, **47**, 733 (1975).
(2) E. D. Goldbert, "Marine Pollution Monitoring: Strategies for a National Program", NOAA, Washington, D.C., 1972.
(3) C. Lee, N. B. Kim, I. C. Lee, and K. S. Chung, *Talanta*, **24**, 241 (1977).
(4) B. G. Stephens, H. L. Felkel, Jr., and W. M. Spinelli, *Anal. Chem.*, **46**, 692 (1974).
(5) A. Zirino and S. H. Lieberman, Chapter in "Analytical Methods in Oceanography", T. R. P. Gibbs, Jr., Ed., *Adv. Chem. Ser.*, **147**, 1975.
(6) K. R. Sperling, *At. Absorpt. Newsl.* **15**, 1 (1976).
(7) P. E. Paus, *Fresenius. Z. Anal. Chem.*, **264**, 118 (1973).
(8) D. A. Segar and J. G. Gonzalez, *Anal. Chim. Acta*, **58**, 7 (1972).
(9) B. P. Fabricand, R. R. Sawyer, S. G. Ungar, and S. Adler, *Geochim. Cosmochim. Acta*, **26**, 1023 (1962).
(10) J. P. Riley and G. Skirrow, "Chemical Oceanography", Vol. III, Academic Press, New York, 1975.
(11) D. C. Burell, *Anal. Chim. Acta*, **38**, 447 (1967).
(12) K. Kremling and H. Peterson, *Anal. Chim. Acta*, **70**, 35 (1974).
(13) J. P. Riley and D. Taylor, *Anal. Chim. Acta*, **40**, 479 (1968).
(14) E. W. Davey and A. E. Soper, Chapter in "Analytical Methods in Oceanography", T. R. P. Gibbs, Jr., Ed., *Adv. Chem. Ser.*, **147**, 1975.
(15) T. M. Florence and G. E. Batley, *Talanta*, **23**, 179 (1976).
(16) T. M. Florence and G. E. Batley, *Talanta*, **24**, 151 (1977).
(17) T. M. Florence and G. E. Batley, *Talanta*, **22**, 201 (1975).
(18) A. S. Douglas and A. Y. Cantillo, Chapter in "Analytical Methods in Oceanography", T. R. P. Gibbs, Jr., Ed., *Adv. Chem. Ser.*, **147**, 1975.
(19) S. Forbug and S. Sundgreen, *Anal. Chem.*, **23**, 1202 (1960).
(20) P. W. J. M. Boumans and F. J. DeBoir, *Spectrochim. Acta*, *Part B*, **31**, 355 (1976).
(21) P. J. Paulsen, private communication.
(22) R. D. Ediger, G. E. Peterson, and J. D. Kerber, *At. Absorpt. Newsl.*, **13**, 61 (1974).
(23) E. C. Keuhner, R. Alvarez, P. J. Paulsen, and T. J. Murphy, *Anal. Chem.*, **44**, 2050 (1972).
(24) J. W. Useller, **NASASP-5074**, Office of Technology Utilization, NASA, Washington, D.C., 1969.
(25) J. A. Dean and T. C. Rains, Ed., "Flame Emission and Atomic Absorption Spectrometry", Vol. 2, Components and Techniques, Marcel Dekker, New York, 1971.
(26) J. R. Moody and R. M. Lindstrom, *Anal. Chem.*, **49**, 2264 (1977).
(27) E. J. Maienthal and D. A. Becker, *Natl. Bur. Stand.* (*U.S.*), *Tech. Note*, **929**, 1976.
(28) J. R. Moody, H. L. Rook, P. J. and Paulsen, T. C. Rains, I. L. Barnes, and M. S. Epstein, *Natl. Bur. Stand.* (*U.S.*) *Spec. Publ.*, **464**, W. A. Kirchhoff, Ed., 1977.
(29) B. Holymaka, *Radiochem. Radioanal. Lett.*, **17**, 313 (1974).
(30) D. E. Leyden and A. L. Underwood., *J. Phy. Chem.*, **68**, 2093 (1964).
(31) M. G. Lai and H. A. Goya, U.S. Naval Radiological Defense Laboratory, Dept. of Commerce, National Technical Information Service, **AD-6486**185, 1966.
(32) C. M. Callahan, J. M. Pascual, and M. G. Lai, U.S. Naval Radiological Defense Laboratory, Dept. of Commerce, National Technical Information Service, **AD-647661**, 1966.
(33) G. H. Luttrel, Jr., C. More, and C. T. Kenner, *Anal. Chem.*, **43**, 1370 (1971).
(34) A. C. Kayser, *J. Chem. Educ.*, **36**, 128 (1959).
(35) R. E. Lapp and H. L. Andrews, "Nuclear Radiation Physics", Prentice-Hall, Englewood Cliffs, N.J., 1959.
(36) J. A. Dean and T. C. Rains, Ed., "Flame Emission and Atomic Absorption Spectrometry", Vol. 3, Elements and Matrices, Marcel Dekker, New York, 1975.

RECEIVED for review July 31, 1978. Accepted September 26, 1978. This paper was taken in part from the dissertation written by H.M.K. and accepted by the graduate school, The American University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry. In order to adequately describe materials and experimental procedures, it was occasionally necessary to identify commercial products by manufacturer's name or label. In no instance does such identification imply endorsement by the National Bureau of Standards nor does it imply that the particular products or equipment is necessarily the best available for that purpose.

APPENDIX 4

FORM NBS-348
(12-65)

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
WASHINGTON, D.C. 20234

June 17, 1981

REPORT OF ANALYSIS

To: H. M. Kingston

Subject: Determination of Cadmium, Copper, Lead, Manganese, and Nickel in Aqueous and Solid Samples from the Chesapeake Bay

Method: Atomic Absorption Spectrometry

Atomic absorption spectrometry (AAS) is a unique analytical technique for the determination of metallic elements. At the present state-of-the-art the method is widely used to determine some 60 elements. For some elements concentrations as low as 10^{-14} g can be detected [1].

The basic components of AAS are the (1) primary source of radiation, (2) production of atomic vapor (flame or electrothermal), (3) wavelength isolator, (4) radiation detector, and (5) readout.

A number of radiation sources are available but the hollow cathode lamp (HCL), in general, is satisfactory for most AAS work. For a few elements which emit radiation in the far ultraviolet region of the spectrum such as arsenic and selenium, electrodeless discharge lamps (EDL) are recommended. EDL's are typically more intense sources of radiation and in a few cases give improved sensitivity over the HCL.

Historically a flame was the original means of producing atomic vapor for AAS. The flame is still the basic source for the vast majority of the AAS measurements [2], and it will probably remain so for the forseeable future. The major advantages of the flame as a means of production of atomic vapor are: (a) simplicity of the technique, (b) speed with which a determination can be made, and (c) relative little maintenance of system. The major disadvantages are (a) a relative large quantity of sample is required for a determination, (b) a hostile environment is created for the production of ground state atoms, (c) large quantities of oxidant and fuel gases are required, and (d) sensitivity is limited for many elements.

In general the concentration of most the trace elements in seawater are below the detection limit of flame atomization systems. Therefore, nonflame or electrothermal atomization (ETA) is generally used. The first furnace device proposed for AAS was that described by L'vov [3]. In his early work, a solution was placed on the end of the electrode and evaporated to dryness. The sample was then vaporized by a dc arc into a carbon furnace. This device produced impressive detection limits but was limited because of power requirements and poor precision.

Massmann [4] constructed a somewhat simpler graphite furnace which is basically being used by all manufacturers today. Interferences encountered with electrothermal atomization devices are more pronounced than in most flame systems, and the analyst has to rely upon the standard addition technique or closely matching of standards with unknown to correct for the interferences. Recent improvements in electrothermal atomization-AAS have greatly reduced analytical interferences. Graphite used in the absorption cell is a porous material which is easily penetrated by liquids and gases. Atomic vapor can freely pass through a 1-mm thick wall of hot graphite. Coating the graphite tubes with a thin layer of pyrolytic graphite has been found to greatly reduce the effects of the porosity of the graphite and increase the sensitivity of some elements. By the inserting of a L'vov platform in the graphite absorption cell, it is possible to atomize the sample at more nearly constant temperature conditions [5]. This reduces analytical interferences by volatilizing the sample into a gas which is hotter than the surface from which the sample is volatilized.

The L'vov platform is available from two of the major AAS instrument manufacturers (Perkin-Elmer Corporation, and Instrumentation Laboratories). While these platforms can be obtained commercially, they can be prepared in the analyst laboratory with a minimum of cost. For the P&E-HGA system, the platforms are constructed by cutting the two ends of a graphite tube into six (three from each end) 7-mm x 5-mm grooved, curved sections. These cuts are made using a small stainless steel saw. After the sections are cut the sides of each section are filed so that the platform will fit the inside contour of the graphite tube.

The graphite tube is positioned in the furnace head. The right window is temporarily removed and the platform inserted. The platform is then centered directly beneath the sample port using a metal rod. Adjustments of the automatic injector tip is made to insure that it does not come into contact with the platform surface.

An essential part of any AAS unit is the monochromator. The monochromator must isolate the analytical line from the various other lines emitted by the source. Failure to resolve the analytical line from all spectral irradiation will result in a loss of sensitivity and nonlinear calibration curve. Another important component of an optical system is the slits to the monochromator. It is desirable that the slit widths be variable as they control the resolution of the monochromator. Normally the analyst operates at a slit width which gives the desired resolution from any adjacent lines. For some analytes the minimum slit width fails to give the desired resolution of the analytical line and, in that case, a tradeoff is made between spectral resolution and sensitivity of the analyte.

The multiplier phototube is widely used as the radiation detector. A list of the most commonly used multiplier phototubes is given by Rains [6].

For readout devices, meters and recorders are popular. Digital readout devices are gaining in popularity and may be considered essential for highly precise work. Advantages are that operator bias in making readings is eliminated, and since the digital device employs a decimal-to-binary or BCD converter on the output, the signal can be fed to a printer or tape punched for subsequent computation on a computer.

ETA-AAS is being widely used for the determination of trace metals in seawater because of its low detection limits and its relative ease of operation [7]. However, concentrations of most trace metals in seawater are often below the detection limit of even the ETA-AAS method. Also, the dissolved solids (3.5 g/L) in seawater may cause serious interference in the determination of many trace elements. Matrix modification is often used to help alleviate the interference associated with high solids; however, this technique was found to be effective only in a few cases. If the trace metal is below the detection limit of ETA-AAS, some form of preconcentration is required. Many studies [2,8-10] have been reported to serve this purpose.

Evaporation is a widely used procedure. It is simple but slow and chemical treatment of the sample is minimized. Only rarely do problems of volability of components or losses on container walls prevent the use of evaporation. However, if the total dissolved solids are high, then preconcentration by evaporation may result in a solution with unacceptably high total solids.

Chelation and solvent extraction is a very common method of concentrating trace metals. One advantage is that unwanted bulk matrix components such as the major salts in sea water are often not extracted. Extraction is rapid and concentration factors of 20-50 can be achieved. For successful extraction the aim is to form a stable complex which has low solubility in the aqueous phase but has high solubility in the organic phase. The organic phase should have limited solubility in water. Problems are encountered with chelation and solvent extraction because the distribution of the complex between the two phase is affected by the pH, the concentration of the organic reagent, the solubility of the complex in the two phases and the ionic strength of the aqueous phase.

Co-precipitation techniques are frequently used to preconcentrate trace elemental concentrations. In this technique the analytes are collected by precipitation on a "carrier-precipitate", which is dissolved in a small quantity of solution. The co-precipitation technique has a number of disadvantages such as lengthy and tedious procedure, and the final solution may contain large quantities of dissolved solids.

Ion-exchange methods, although very time-consuming, can be used to concentrate many metal ions. Columns can be made in any desired size, from a few cubic millimeters up to columns of many cubic meters. The diameter of the column depends on the amount of material to be treated; the length depends on the difficulty of the separation to be accomplished. Ion-exchange resins are porous insoluble 3-dimensional polymeric compounds, usually in the form of powder or small beads. They include firmly bonded organic functional groups. Associated with these functional groups are ions, either cation or anions, which can be exchanged for ions in solution. A description of the various anion and cation exchange resins is given by Dean [11]. Kingston et.al., [12] used Chelex 100 resin and ETA-AAS to determine Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn in estuarine water from the Chesapeake Bay and seawater from the Gulf of Alaska.

Procedure

A. Aqueous

A test portion of the estuarine sample from the Chesapeake Bay was preconcentrated by H. M. Kingston and E. S. Beary using the method described by Kingston et al., [12]. The eluate from this separation which is 2.5 M HNO_3 was analyzed directly for the analytes by ETA-AAS using the L'vov platform. To check for chemical interferences, the single standard addition method was used [2]. The instrumental conditions for each element are given in Table 1.

B. Solids

The solids which were collected on 0.45 μm filter paper were prepared by transferring the filter paper to a Teflon beaker. Then, five mL of HNO_3 and one mL of Hf were added and solution warmed. After the paper had decomposed, five mL of $HClO_4$ was added and sample solution evaporated to near dryness. The solids were then dissolved in one mL of HNO_3 and five mL of water and then transferred to 10 mL volumetric flask. The analytes were determined by ETA-AAS using the instrumental conditions described in Table 1. The recovery of each analyte was checked by the single addition method [2].

References

[1] L'vov, B. V. Atomic Absorption Spectrochemical Analysis, Adam Hilger, London; 1970.

[2] Dean, J. A. and Rains, T. C., eds., Flame Emission and Atomic Absorption Spectrometry, Vol. 3. Marcel Dekker, New York; 1975.

[3] L'vov, B. V. Inzhenerno-Fizicheskii Zhurnal, 2, 44-52 (1959).

[4] Massmann, H. Spectrochimica Acta, 23B, 215-226 (1968).

[5] Slavin, W. and Manning, D. C., Anal. Chem., 51, 261-261 (1979).

[6] Rains, T. C., Special Technical Publication 443, American Society for Testing and Materials, 1969.

[7] Horlick, G., Anal. Chem., 52, 290R-305R (1980).

[8] Riley, J. P. and Taylor, D., Anal. Chim. Acta, 40, 479 (1968).

[9] Muzzarelli, R. A. A. and Rocchetti, R., Anal. Chim. Acta, 69, 35 (1974).

[10] Nix, J., Goodwin, T., At. Absorp. Newsl., 9, 119 (1970).

[11] Dean, J. A., Chemical Separation Methods, Van Nostrand Reinhold, New York, 1969.

[12] Kingston, H. M., Barnes, I. L., Brady, T. J., Rains, T. C., Anal. Chem., 50, 2064 (1978).

T. C. Rains

T. C. Rains, Research Chemist

T. A. Rush

T. A. Rush, Chemist

T. A. Butler

T. A. Butler, Chemist

Ernest L. Garner

E. L. Garner, Chief
Inorganic Analytical Research Division
Center for Analytical Chemistry

Attachments 2

Table 1. Instrumental Parameters.

		P & E 603			HGA - 2200[a]		
Element	Wavelength nm	SBW nm	Scale Expansion	Gas	Drying[c] T-sec	Charring[c] T-sec	Atomization T-sec
Cd[b]	228.8	0.7	2	Ar	125 - 40	800 - 40	2300 - 6
Cu	324.7	0.7	2	Ar	125 - 40	700 - 40	2600 - 6
Mn	279.5	0.7	2	Ar, Stop Flow	125 - 40	800 - 40	2700 - 6
Ni	232.0	0.7	5	Ar	125 - 40	800 - 40	2700 - 6
Pb[b]	283.3	0.7	3	Ar	125 - 40	800 - 40	2400 - 6

---

[a] With L'vov Platform.

[b] $(NH_4)_2HPO_4$ used in matric modification.

[c] Ramp mode used for first 20 seconds.

Table 2. Control Samples.

Sample	Pb	Ni	Cu	Cd
		ng/mL		
TWS -1	33	--	16, 19 17, 18 17, 19	12
-2	26 28	--	--	11
-3	27	--	14	10
-4	27 26 27	56	13	13
-5	27 31 27	--	13	11
-6	27 29	49 53 48	14 16	
Average =	28	52	16	11
Std. Dev. =	2.1	3.4	2.2	0.8
Rel. Std. Dev. % =	7.6	6.5	14	7.4
Control, SRM 1643a, Certified Values	27 ± 1	55 ± 3	18 ± 2	10 ± 1

APPENDIX 5

APPENDIX 5

BLANK UNCERTAINTIES AND CORRECTIONS

Correction for the analytical blank must be made along with two other corrections, one for chemical retention and the other for the volume change upon sample acidification. The correction for the analytical blank is the correction for any contamination picked up during sample handling and analysis. This correction is the most complicated of the three because the contamination is modeled as random. For each element and each sample type, the distribution of the measurements on the blank is obtained. This distribution is used to predict the contamination in the Bay samples and thus to correct for it. Because the prediction of a random variable is involved, this correction increases the uncertainty, sometimes considerably. The other two corrections involve only scaling the results.

Each measurement is presented in two ways, as a point estimate of the quantity and as an interval estimate that is approximately at the 95% confidence level. Note that this summary of the Bay measurements may not be adequate for all purposes. The Bay measurements will be used in various ways to draw conclusions: two measurements will be compared, two ratios of measurements will be compared, the maximum measurement will be compared to the others, and the average of the measurements from some region will be compared with measurements from another region. In each of these cases, whether the difference observed could be caused by measurement error must be investigated. The proper answer to this question involves, among other things, the measurement-to-measurement dependence of the measurement error. However, the point-estimate, interval-estimate summary is useful. It provides a basis for conclusions when the differences observed are much larger than the measurement error.

Correction for the blank involves three steps. First, the blank measurements are modeled. This consists of exploratory analysis, estimation of a transformation to normality, determination of any dependence on the batch in the case of the dissolved samples, and determination of any dependence on the number of filters in the case of the particulate samples. Second, the model for the blank measurements is used to find a point estimate and a one-sided or two-sided prediction interval for the blank contribution to the Bay samples. This is done ignoring the uncertainty due to estimation of the transformation from the data. Third, these predictions are combined with the uncorrected measurements each of which is accompanied by the standard deviation of its measurement error. This combination is done in various ways depending on whether the blank measurements are normal or not, depending on whether the prediction interval is one-sided or two-sided, and depending on how many of the blank measurements are below the detectable limit. When the blank measurements are not normal, the Bonferroni inequality is used. When most of the blank measurements are below detectable limits, the procedures are somewhat ad hoc and depend on the magnitude of the detection limits compared to the concentrations observed.

THE BLANKS

Organization

The measurements that are included in this work conclude the accumulation of concentration data obtained from samples collected during the 1979 cruise sampling the Chesapeake Bay. Each elemental blank of each type sample, particulate and dissolved, was modeled and adjusted using the following procedures. The data base for the numbers was the raw data uncorrected from the instruments. Due to the complex nature of the blank and sample relationship the computerized blank corrections were rigorous and required an individual treatment by element. These blank influences are unique for each element and for each type of sample of each element (particulate or dissolved), and occasionally are influenced by the group or batch in which they were chemically manipulated in the separation and concentration procedures. These factors and other considerations contributed to an individual statistical model for each elemental blank of the two sample types. This procedure was necessary for a complete and adequate assessment of the blank contribution of the concentrations analyzed.

The blank values with uncertainties also appear as discrete data and are themselves important and are input and maintained with the data for future reference.

Each element was treated individually and the statistical evaluation and mathematical manipulation necessary to correct the average value for the blank and uncertainty was addressed. In some cases the blank was relatively insignificant in relation to the levels of the element of interest. In other instances the level of the blank was below detectable limits and was evaluated with the understanding that the limit of detection was an upper limit below which the concentration of the blank exists unknown.

The total data base for the entire project is organized as follows:

TABLE I. ORGANIZATION OF DATA

Elements Determined in the Particulate Portion of the Sample	Elements Determined in the Dissolved Portion of the Sample	Instrumental Method of Determination
Data Subset A	Data Subset B	
Ce Co Cr Fe Mo Sc Sn Th U Zn	Co Cr Fe Mo Sc Sn Th U Zn	Neutron Activation Analysis (NAA)
Data Subset C	Data Subset D	
Cd Cu Mn Ni Pb	Cd Cu Mn Ni Pb	Graphite Furnace Atomic Absorption Spectrometry (GFAAS)

Blank Corrections

There are several reasons for the need of a more refined method of handling blank contribution than are traditionally utilized. The blanks are significant for several elements. The origin of the blank concentration dictate the statistical treatment of the blank. There are several sources of blank contribution and also more than a single statistical relationship for the concentration range of the blanks. Therefore, it is necessary to establish a statistical model for each elemental blank to arrive at a statistically accurate mean value and uncertainty range that is known within the desired confidence limit and which produces, after subtraction, a corrected concentration with uncertainties that are at least at the 95 percent confidence limit.

Each element of the sample type (dissolved and particulate) is discussed separately. Each blank model is presented and the subsequent mathematical manipulation documented. A detailed mathematical procedure follows describing the statistical form of correction, its magnitude and some explanations, where relevant, to specify the blank procedure used in each case.

Cobalt; Dissolved (Data Subset B)

The model of the blank was log normal with a 0.0045 ng/mL shift, $\log(X_{ij}-0.0045) \sim N(\mu,\sigma^2)$. This should be read: the logarithm of the blank values X_{ij} minus 0.0045 ng/mL was normally distributed N with mean μ and variance σ^2. This model suggested two sources of Co, one at 0.0045 ng (possibly from the irradiation film or the resin) underlying the other contributing source distributed log normally.

The point prediction P was 0.0091 ng/mL with a lower limit L=0.0049 ng/mL and upper limit U=0.0659 ng/mL.

Since subtraction of a blank was required, adjustment of the uncertainties was made to the 97.5 percent confidence limit to produce an after manipulation of at least the 95 percent confidence limit. The adjustment of the confidence limit from one sigma to 97.5 percent was accomplished by equation 1.

$$C-2.24\sigma,\ C,\ C+2.24\sigma \qquad (1)$$

where C was the uncorrected concentration and σ represented the uncertainty given to C. To produce the blank correction and adjust the confidence limits in one step, equation 2 was used with the upper limit (U) subtracted from $C-2.24\sigma$, the point prediction (P) was subtracted from C and the lower limit (L) was subtracted from $C+2.24\sigma$:

$$[(C-2.24\sigma)-U],\ (C-P),\ [(C+2.24\sigma)-L] \qquad (2)$$

If the minimum value thus obtained is less than zero, the situation in which the observed concentration could not be distinguished from contamination at the 2.5 percent level occurs. In this case, the minimum value was replaced by zero. Also, any other values that were less than zero were replaced by zero.

Iron; Dissolved (Data Subset B)

The iron blank was modeled by $\log(X_{ij}-0.4) \sim N(\mu,\sigma^2)$. The point prediction was P=1.12 ng/mL with lower limit L=0.56 ng/mL and upper limit U=3.68 ng/mL. Equation 2 produced a corrected value with limits at least at the 95 percent confidence limit.

Lead; Dissolved (Data Subset B)

The blanks were modeled by a log normal distribution $\log(X_{ij}) \sim N(\mu,\sigma^2)$ with a point prediction of 0.133 ng/mL and a lower limit of 0.0563 ng/mL and an upper limit of 0.316 ng/mL. Utilizing equation 2 produced corrected values with limits at least at the 95 percent level.

TYPING GUIDE SHEET

Thorium; Dissolved (Data Subset B)

The thorium blank values were distributed log normally $\log(X_{ij}) \sim N(\mu,\sigma^2)$ and had a point prediction P of 0.0004 ng/mL and a lower limit L=0.0000 ng/mL with an upper limit of U=0.0044 ng/mL. Due to the non-computation of the lower limit L, a modification to that side of the equation 2 was made which resulted in eliminating the need to have a 2.5 percent uncertainty reserve for computational purposes. Thus the equation used for the adjustment of thorium was as follows:

$$[(C-2.24\sigma)-U],\ (C-P),\ [(C+1.96\sigma)-L] \qquad (3)$$

The values adjusted in this manner resulted in blank corrected data with an uncertainty of at least the 95 percent confidence limit.

Copper; Dissolved (Subset D)

The copper blank data was modeled in a log normal manner. $\mathrm{Log}(X_{ij}) \sim N(\mu,\sigma^2)$ with a point prediction of 0.06 ng/mL and lower limit L=0.00 with an upper limit U=0.84 ng/mL. The handling of these blanks was similar to that of the dissolved thorium. The use of equation 3 was implemented.

Chromium; Dissolved (Data Subset B)

The model for the chromium blank was normally distributed, $X_{ij} \sim N(\mu,\sigma^2)$. The point prediction P was 1.55 ng/mL with a standard deviation σ_b of 0.10 ng/mL. In this case the concentration uncertainties and the blank values were both modeled normally. Thus, another form for the correction procedure resulted.

Correction for the chromium blank was accomplished by subtracting P from C, C-P. The correction of the uncertainties to at least the 95 percent confidence limit was accomplished by substituting σ (the reported analytical uncertainty) in the following equation for each concentration uncertainty. A return to the symmetrical normal form was possible for chromium, see equation 4.

$$(C-P) \pm 1.96\sqrt{\sigma^2+\sigma_b^{\,2}} \qquad (4)$$

This was a result of the majority of the chromium being contributed by the LPE irradiation film in which the sample was sealed, and thus it was logical to have obtained a normal distribution.

Scandium; Dissolved (Data Subset B)

The blanks were normally distributed for scandium following $X_{ij} \sim N(\mu,\sigma^2)$ with point prediction P=0.00012 ng/mL. The standard deviation σ was 0.00004

EPA-287 (Cin.)
(4-75)

ng/mL and was treated in a similar manner as the chromium. Equation 4 was utilized in the adjustment of the concentration data to at least the 95 percent confidence limit.

Batch Preparation Blank Dependence

In the preparation of the dissolved samples for both NAA and GFAAS analyses the chemical manipulation was complex and time consuming. The time required to prepare each sample necessitated a batch organization. The batches were usually organized in numerical order. At this time the batch blanks, standards and corresponding blank filter numbers corresponding to the samples being prepared were also prepared. In the statistical analyses of the blanks and samples the batch dependence of this preparation was also checked statistically. It was found to be significant in a few cases and in these cases a within batch point prediction P, lower limit L, and an upper limit U were calculated. For both data base set B and D the sample numbers were coded to include their batch run number for example 11,001 1, Blank 9 1 and 11,001B 1, were all prepared in batch run number 1. The last digit coming after the space for both data set B and D indicated the batch in which it was prepared. There were 8 batches and where a run dependence was statistically significant the element had a set of P, L, and U values for that batch.

Nickel; Dissolved (Data Subset D)

There was observed a statistically significant batch preparation blank component for nickel. The blank values for nickel were log normally distributed $\log(X_{ij}) \sim N(\mu_j, \sigma^2)$. The P, L and U values are given in Table II.

TABLE II. THE P, L, AND U VALUES FOR THE DISSOLVED NICKEL BLANK CORRECTIONS

	- - - - - - - Concentration in ng/mL	- - - - - - -	
Batch Number	Point Prediction P	Lower Limit L	Upper Limit U
1	0.05	0.02	0.18
2	0.04	0.01	0.12
3	0.23	0.07	0.77
4	0.18	0.05	0.62
5	0.06	0.02	0.20
6	0.06	0.02	0.21
7	0.23	0.07	0.78
8	0.10	0.03	0.32

These P, L, and U values were treated as other blank corrections with a mathematical operation following equation 2. The only difference was the use of the P, L, and U corresponding to the same batch number rather than using a single point and limits for all batches.

Zinc; Dissolved (Data Subset B)

The zinc blanks were modeled using a log normal distribution with a starter component $\log(X_{ij}+1.0) \sim N(\mu_j,\sigma^2)$. The batch component dependent point predictions and limits appear in Table III.

TABLE III. THE P, L, OR U VALUES FOR THE DISSOLVED ZINC BLANK CORRECTIONS

	- - - - - - - Concentration in ng/mL - - - - - - -		
Batch Number	Point Prediction P	Lower Limit L	Upper Limit U
1	0.56	0.00	2.12
2	0.88	0.00	2.76
3	0.80	0.00	2.60
4	1.21	0.11	3.42
5	1.09	0.05	3.18
6	1.57	0.29	4.14
7	1.73	0.37	4.45
8	3.05	1.02	7.08

The treatment of these blank corrections and adjustments of the uncertainty on the concentration was as described previously. Batches 1 through 8 were adjusted using equation 2.

Manganese; Dissolved (Data Subset D)

The manganese blanks were modeled using a normal distribution and demonstrated a batch dependency $X_{ij} \sim N(\mu_j,\sigma^2)$. The P, L, and U values are presented in Table IV.

TABLE IV. THE P, L, AND U VALUES FOR THE DISSOLVED MANGANESE BLANK CORRECTIONS

	- - - - - - - Concentration in ng/mL - - - - - - -		
Batch Number	Point Prediction P	Lower Limit L	Upper Limit U
1	0.56	0.20	0.93
2	0.73	0.37	1.10
3	0.00	0.00	0.008
4	0.36	0.00	0.72
5	0.18	0.00	0.56
6	0.00	0.00	0.008
7	0.69	0.25	1.13
8	0.00	0.00	0.008

The treatment of these blank corrections and adjustment of the uncertainty on the concentration was as described previously. Batches 1 through 8 were adjusted using equation 2.

Concentrations Needing No Blank Correction

Molybdenum, Tin, and Uranium; Dissolved (Data Subset B)
Cadmium; Dissolved (Data Subset D)
Manganese; Particulate (Data Subset C)

For each of these elements the blank contribution to the measurement was undetectable in almost all blank samples. It was therefore statistically impossible to provide even the most minute correction resulting from a blank component in the given concentrations. It was also not possible to project the probability increase in the limits of the concentrations given.

However, this was not significant for uranium, molybdenum, or manganese where a consistent measurement two to three orders of magnitude above the limit of detection was uniformly measured for the samples. Any blank correction given these conditions was insignificant. Therefore supposing the lower limit of detection to be its maximum upper level, no blank correction was necessary.

For cadmium and tin the majority of the samples were below the detection limits. There were no tin values for any blanks and statistically no evaluation could be made. The observation that the blanks for tin were all below the lower limit of detection gave confidence that the measured concentrations for the samples were significant levels of tin and were real observations, not artifacts of a variable blank.

There were four cadmium blanks observed just above the detection limit. The data were not strong enough to support a consistent blank at or above the detection limit of the instrument and no blank correction could be attempted for cadmium.

Although no blank correction was needed it was necessary to adjust the upper and lower limits of the data to at least the 95 percent confidence limit. To accomplish this equation 5 was used.

$$C-1.96\sigma, C, C + 1.96\sigma \tag{5}$$

Copper; Particulate (Data Subset C)

This statistical treatment was applied to copper and a dependence on the number of filters used in the sample collection was found to be a significant contributing factor to the blank concentration. As in previous work of this type the P, L, and U were dependent upon the number of filters for that sample. The number of filters for each sample is given in Appendix 1. It was found that there was no significant dependence related to the type of filters, therefore only the numbers of filters used to collect the sample was significant. Table V provides the P, L, and U used for the blank correction.

To correct the concentrations for blank and obtain the uncertainties to at least the 95 percent confidence limit equation 2 was used.

TABLE V. THE P, L, AND U VALUES FOR THE PARTICULATE COPPER BLANK CORRECTION

Number of Filters	Concentration in ng/mL Point Prediction P	 Lower Limit L	 Upper Limit U
1	0.23	0.08	0.45
2	0.46	0.23	0.76
3	0.68	0.39	1.06

Lead; Particulate (Data Subset C)

Since only a few blank levels were marginally above the lowest limit of detection the blank values were influencing only a small number of the concentrations obtained. Although a blank correction was not warranted for the concentrations, an uncertainty of a magnitude comparable with the blank influence was included. This was accomplished by increasing only the lower uncertainty. Using an upper limit U = 0.04 ng/mL and adjusting the data to at least the 95 percent confidence limit using equation 6 produced a conservative treatment for the data.

$$[(C-2.24\sigma)-U],\ C,\ C + 1.96\sigma \tag{6}$$

Nickel; Particulate (Data Subset C)

Reasoning similar to that for the lead particulate data led to a similar treatment where U = 0.09 ng/mL. Applying this in equation 6 yielded a confidence limit of at least the 95 percent confidence limit.

Zinc; Particulate (Data Subset A)

The blanks for zinc consisted of 1, 2 or 3 filters. Since the data showed clearly that the amount of contamination depended on the number of filters, a model for the dependence of the contamination on the number of filters was needed. Contamination might have increased with the number of filters because the filters themselves introduce contamination and because more handling is needed for more filters. Thus, the contamination might have been modeled as the sum of 1, 2 or 3 independent random variables depending on how many filters are in the blanks. With this model, the mean and the variance of the contamination were both proportional to the number of filters. That the variance was proportional to the mean suggested the use of the square root transformation to obtain data for which the variance did not depend on the number of filters. In figure 1, the square root of the contamination was plotted versus the square root of the number of filters. A linear relation between the two square roots was plausible but the data were

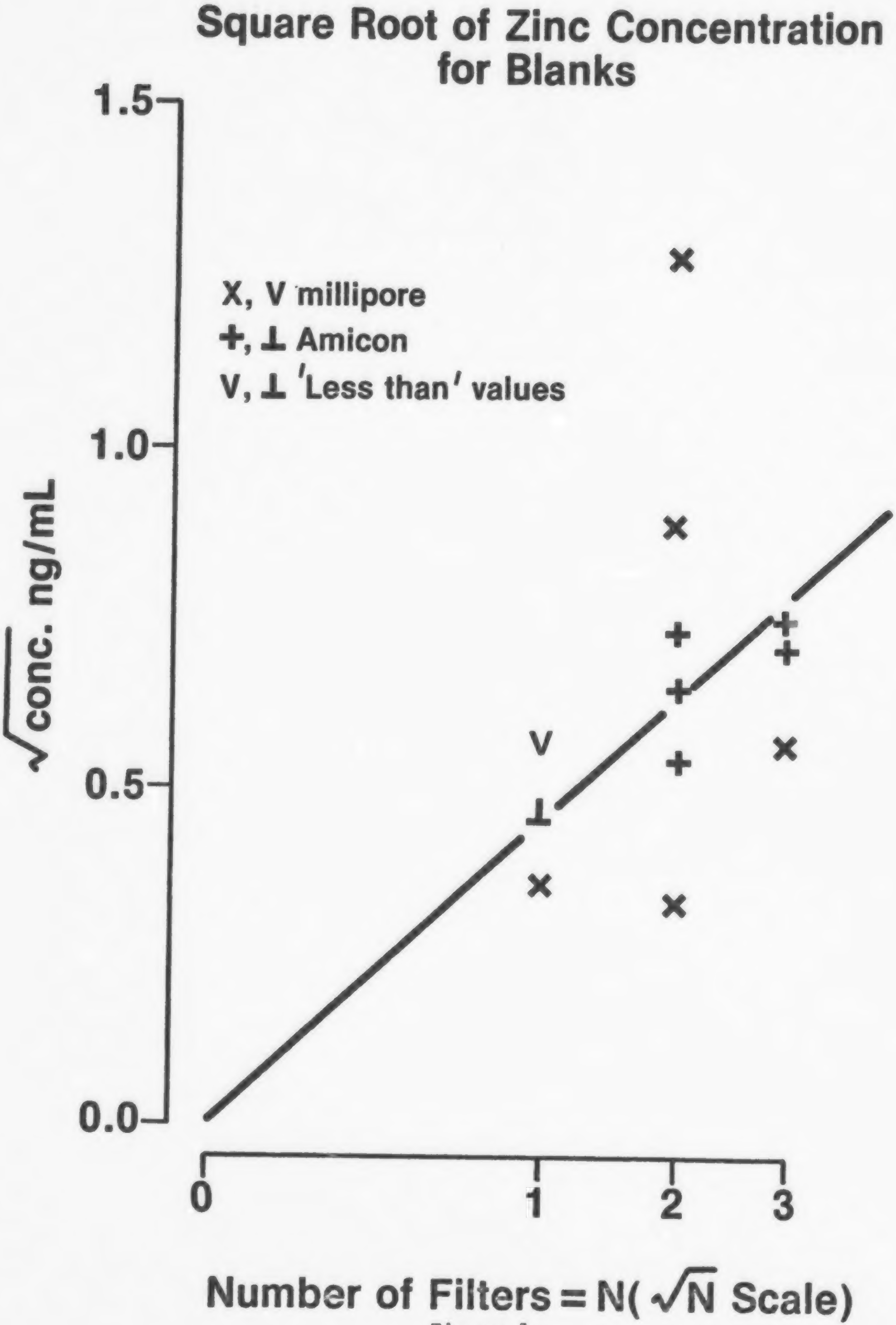
Square Root of Zinc Concentration for Blanks
1.5
1.0
0.5
0.0
√conc. ng/mL
X, V millipore
+, ⊥ Amicon
V, ⊥ 'Less than' values
V
⊥
0
1
2
3
Number of Filters = N(√N Scale)

Figure 1.

insufficient to provide any support for the hypothesis of constant variance. Note that two different filters, Millipore and Amicon, were represented but could not be distinguished.

Let Z be the amount of contamination and N the number of filters. The model

$$\sqrt{Z} = \beta\sqrt{N} + \varepsilon \qquad (7)$$

was fit by ordinary least squares giving the following predictions for the amount of contamination in the real samples.

TABLE VI. THE P, L, AND U VALUES FOR THE PARTICULATE ZINC BLANK CORRECTION

	------ Concentration in ng/mL -------		
Number of Filters	Point Prediction P	98.75% Confidence Limits	
		L	U
1	0.20	0	1.30
2	0.41	0	1.80
3	0.61	0	2.27

To obtain limits for the zinc measurements that were at least at the 95% confidence level, the original values denoted by $C \pm \sigma$ were used to obtain 96.25% confidence limits for the concentrations uncorrected for the blanks

$$C - 2.24\sigma,\ C,\ C + 1.96\sigma \qquad (8)$$

Then, subtraction of the upper limit (U) on the blank from $C - 2.24\sigma$, the point prediction (P) from C, and the lower limit (L) on the blank from $C + 1.96\sigma$ as indicated in equation 8 yielded equation 3.

$$[(C-2.24\sigma)-U],\ (C-P),\ [(C+1.96\sigma)-L] \qquad (3)$$

The values for P, L, and U corresponded to the number of filters used for the sample being operated upon. If the minimum value thus obtained was less than zero, the situation existed in which the observed concentration could not be distinguished from contamination at the 2.5% level. In this case, we replaced the minimum value by zero. Also, any other values that were less than zero were replaced by zero.

Chromium; Particulate (Data Subset A)

Our analysis for chromium was the same as that for zinc (Data Subset A) with two exceptions. First, the polyethylene bag that contained the filters contributed 0.07 ng to the concentration as seen from the measurements on the bag alone. Thus, subtraction of 0.07 ng before taking the square root was necessary. The result which is plotted in figure 2 shows clearly that the Millipore filters contained less chromium than the Amicon filters, suggesting that the filters and not the handling contributed the chromium. This idea was supported by the values for the filters that were not subject to handling. For this reason, separate relations for each filter type were fitted. Figure 2 shows that the variance for the Amicon filters was larger (the F-test is significant at the 0.01 level). Nevertheless, the sums of squares were pooled to estimate the variances. This pooling was based on the assumption that each set of filters had the same uniformity and was subject to the same contamination mechanisms.

To correct the concentrations for blanks and obtain the uncertainties to at least the 95% confidence limit, equation 2 was used.

$$[(C-2.24\sigma)-U],\ (C-P),\ [(C+2.24\sigma)-L] \qquad (2)$$

TABLE VII. THE P, L, AND U VALUES FOR THE PARTICULATE CHROMIUM BLANK CORRECTION

	- - - - - Concentration in ng/mL - - - - -		
	MILLIPORE		
N	Point Prediction P	97.5% Confidence Limits L	 U
1	0.18	0.12	0.46
2	0.35	0.21	0.72
3	0.53	0.33	0.97
	AMICON		
1	0.71	0.48	1.17
2	1.43	1.04	2.04
3	2.14	1.62	2.89

Iron; Particulate (Data Subset A)

For iron the square root of the iron measurement was normally distributed with mean 1.04 ng/mL and standard deviation of 0.4 ng/mL we conclude that the contamination might be as high as 3.7 ng/mL (at the 97.5% limit). Because the data on the contamination is so sketchy (due to 'less than' values predominating), the measurements and their upper limit are not adjusted for contamination. The lower limit was reduced by 3.7 ng/mL to account for the possibility of contamination. The upper limit, point prediction, and lower limit were calculated as follows:

$$[(C-2.24\sigma)-3.7],\ C,\ C+1.96\sigma \qquad (11)$$

This gave at least a 95% confidence limit. Any minimum value less than zero after adjustment was adjusted to zero as a negative was not possible.

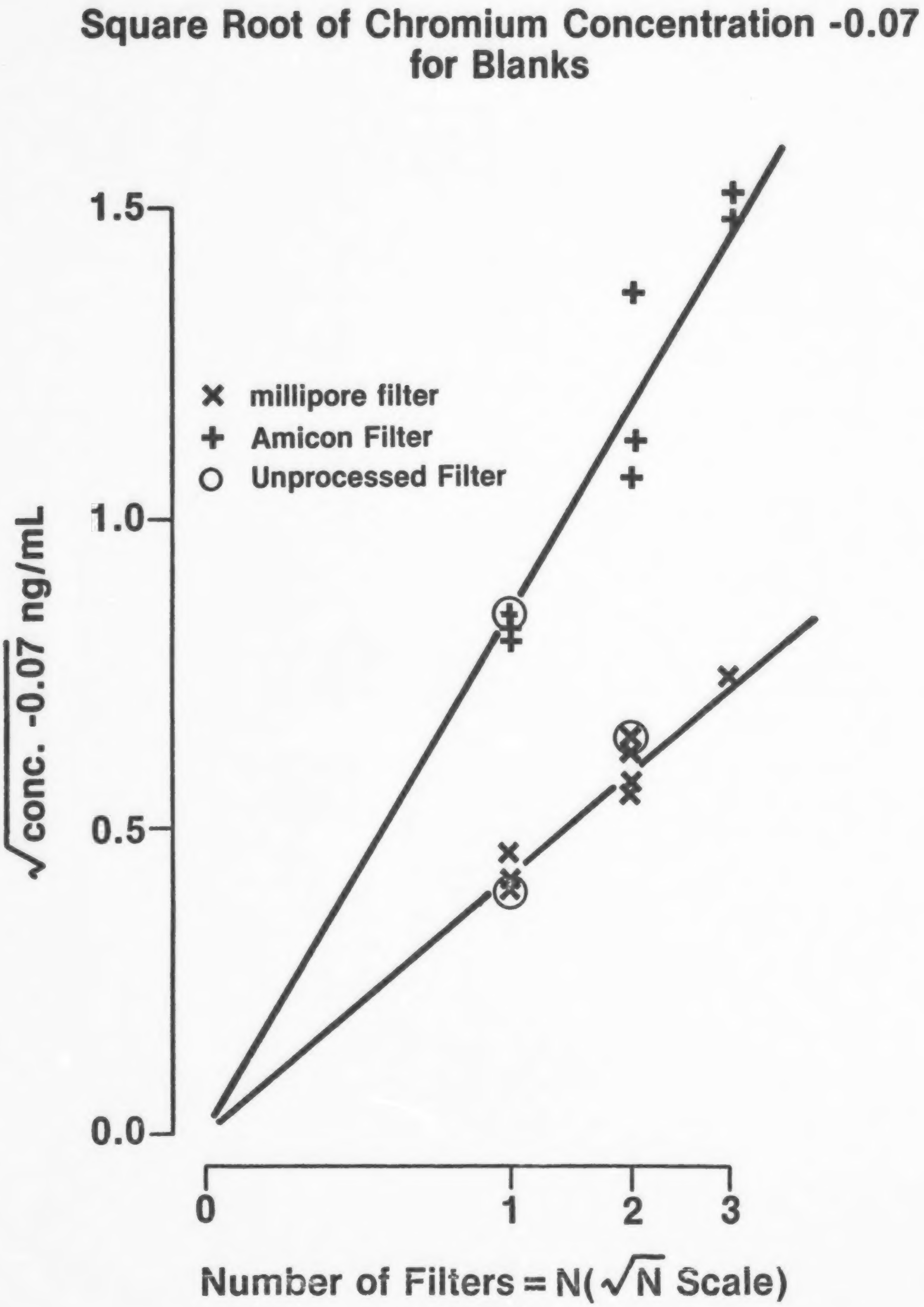
Square Root of Chromium Concentration -0.07 for Blanks
1.5
1.0
0.5
0.0
$\sqrt{\text{conc.}}$ -0.07 ng/mL
× millipore filter
+ Amicon Filter
○ Unprocessed Filter
0
1
2
3
Number of Filters = N($\sqrt{N}$ Scale)

Figure 2.

Scandium; Particulate (Data Subset A)

. . . we conjecture that the square root of scandium measurements might be modeled as normal with mean 1.14×10^{-2} and standard deviation 1.14×10^{-2}. This suggests that the contamination might be as high as 0.0013 ng/mL as with iron this value could be subtracted from the lower limit on the values for the real samples. The highest observed blank value was half this amount. The samples were adjusted to yield a final 95% confidence limit overall.

$$C-1.96\sigma,\ C,\ C + 1.96\sigma \tag{12}$$

Fortunately, most measurements on the real samples were well above the observed contamination values.

Uranium; Particulate (Data Subset A)

For uranium, the blanks are all reported as 'less than' values. These values, which are quite variable, reflect primarily the background levels rather than the uranium levels. All that can be said is that the contamination observed in the blanks does not exceed 0.02 and that the contamination may be orders of magnitude less than 0.02. Unfortunately, the uranium values for several real samples are less than 0.02. For these samples, the possibility that the observed levels are due to contamination cannot be objectively ruled out. A user of the uranium values should be warned of this problem, but no correction of the uranium values for the contamination was applied.

To adjust the upper limit and lower limit to yield a final confidence limit of 95%, the samples were adjusted as follows:

$$C - 1.96\sigma,\ C,\ C + 1.96\sigma \tag{13}$$

This was appropriate because no blank adjustment was necessary.

Cerium, Cobalt, Thorium and Molybdenum; Particulate (Data Subset A)

For cerium, cobalt, thorium and molybdenum, we can do little but observe that the blank values observed are certainly less than 0.038 for Ce, 0.017 for Co, and 0.003 for Th. Correction for the blank was suggested since the data are too limited to allow any model of the contamination to be surmised. Fortunately, most measurements on the real samples are well above the observed blank values.

To adjust the upper limit and lower limit to yield a final confidence limit of 95%, the samples were adjusted as follows:

$$C - 1.96\sigma,\ C,\ C + 1.96\sigma \tag{5}$$

This was appropriate because no blank adjustment was necessary.

TYPING GUIDE SHEET

The Correction for Chemical Retention of the Dissolved Concentrations

As published in the 1978 article by Kingston, et al., the retention of the elements was either quantitative or had a reproducible recovery. These recoveries which have been documented in the 1978 Analytical Chemistry article including Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn as applicable to sea, estuarine, and fresh water utilizing GFAAS as the analyzing instrument (1).

The other elements of interest Cu, Mo, Sc, Sn, Th, and U were tested for their recoveries to calibrate the technique for these elements. The retentions applicable to these analyses are given collectively in Table VIII.

TABLE VIII. THE RETENTION OF SELECTED TRACE ELEMENTS DONE BY NAA OR GFAAS AS DIRECTLY APPLICABLE TO THESE SAMPLES (UNCERTAINTIES AT THE ONE SIGMA LEVEL)

Element	Percent Retention (R)
Cd	99.99 ± 0.071
Co	99.5 ± 0.3
Cr	94.94 ± 0.33
Cu	99.97 ± 0.03
Fe	93.1 ± 2.2
Mn	99.99 ± 0.11
Mo	98.38 ± 0.19
Ni	99.91 ± 0.083
Pb	98.4 ± 0.48
Sc	84.84 ± 0.22
Sn	83.85 ± 0.16
Th	82.83 ± 0.34
U	98.8 ± 0.2
Zn	99.96 ± 0.097

The percent retentions in Table VIII were used to correct the concentrations of the dissolved samples of data subsets B and D, after the blank values had been subtracted. They were, however, not applicable to the particulate samples in data subsets A and C and were not applied to these data subsets.

The statistical uncertainty of these corrections for each element was evaluated and shown to be insignificant when compared to the instrumental uncertainties, the blank contribution and the conservative arithmetic handling of the data. Application of the uncertainties at this time could result in a rounding error more significant in most cases than the uncertainty of these retentions.

The correction was made for each best value and its lowest and highest estimate using the form $x = \frac{y}{R}$ where x was the final concentration adjusted for

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retention, blank, and which was at least at the 95 percent confidence limit; R was the fractional retention in decimal form; and y was the concentration after blank correction and 95 percent adjustment.

There were certain elements in the dissolved data subsets B and D for which the correction was unnecessary due to the completeness of the retention. These elements were: Cd, Co, Cu, Ni, Mn, U, and Zn. Therefore the retention corrections were made on Cr, Fe, Mo, Pb, Sc, Sn, and Th only.

These corrections were carried out in such a way as to make use of the computer memory storage of additional significant figures from previous operations. The rounding error was minimized by only rounding after the last computation had been completed, only then returning to the original number of significant figures. Example:

$$x = \frac{9.200}{0.8283} = 11.11, \quad x = \frac{10.00}{0.8283} = 12.02, \quad x = \frac{11.00}{0.8283} = 13.28$$

This was the last adjustment step for the dissolved data subset D and these concentrations were rounded to the original number of significant figures. Following the example each concentration had two significant figures and was returned to two significant figures i.e., 11, 12, and 13 ng/mL, respectively.

Adjustment for Volume

There remained an adjustment that was applied to the particulate subset A and dissolved subset B concentrations only. This factor was applied to sample concentrations and range but not to any less than upper limit values or blank values. This correction arose from a volume change due to the acid added for stabilization of the samples.

The ratio to be multiplied was

$$\frac{1062.5}{1033.1} = 1.0285$$

This correction was made on data sets C and D during the analysis by GFAAS.

The Final Form

These aforementioned manipulations adjusted the concentration data to at least the 95 percent confidence limit, compensated for blank and retention were applied where necessary, producing a data set in final form.

Two types of data information were left uncorrected after these manipulations, the blanks themselves and the less than numbers. Both of these groups were preserved in their original form, i.e., the blanks and less than numbers did not have blank correction manipulations operated upon them. The blanks were maintained in separate data files by element and sample type with their uncertainties. The less than values were also maintained but with the other concentration data indexed by sample number. They did not, however, lose their identity as less than numbers and, when retrieved, were retrieved as a less than with no discrete mean value or uncertainties.

LITERATURE CITED

(1) Eisenhart, Churchill, "Expression of the Uncertainties of Final Results" NBS Special Publication 300, Vol. 1, page 69-1201 (1969).

(2) Currie, Lloyd A. "Limits for Qualitative Detection and Quantitative Determination, Application to Radiochemistry" Anal. Chem., 1968, 40 (enclosed).

APPENDIX 6

Table 1

THE CONCENTRATION OF DISSOLVED CADMIUM
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER		MINIMUM	BEST VALUE	MAXIMUM
11102	8		< 0.007	
11101	8	0.081	0.101	0.121
11100	8	0.050	0.062	0.074
11099	8	0.020	0.024	0.028
11098	8	0.077	0.095	0.113
11097	8	0.034	0.042	0.050
11096	8		< 0.007	
11095	7		< 0.007	
11094	7		< 0.007	
11093	7		< 0.007	
11092	7	0.069	0.087	0.105
11091	7	0.048	0.060	0.072
11090	7	0.014	0.018	0.022
11089	7	0.068	0.086	0.104
11088	7	0.035	0.045	0.055
11087	7	0.043	0.053	0.063
11086	7	0.067	0.083	0.099
11085	7	0.035	0.045	0.055
11084	7		< 0.007	
11083	7		< 0.007	
11082	7		< 0.007	
11081	7	0.030	0.038	0.046
11080	6	0.059	0.073	0.087
11079	6		< 0.007	
11078	6	0.069	0.087	0.105
11077	6	0.068	0.084	0.100
11076	6	0.067	0.083	0.099
11075	6	0.050	0.062	0.074
11074	6	0.038	0.048	0.058
11073	6	0.026	0.032	0.038
11072	6	0.033	0.041	0.049
11071	6		< 0.007	
11070	6		< 0.007	
11069	6	0.025	0.031	0.037
11068	6	0.024	0.030	0.036
11067	5	0.043	0.055	0.067
11066	5		< 0.007	
11065	5		< 0.007	
11064	5	0.035	0.045	0.055
11063	5		< 0.007	
11062	5	0.029	0.037	0.045
11061	5	0.019	0.023	0.027
11060	5	0.025	0.031	0.037
11059	5		< 0.007	
11058	5	0.020	0.024	0.028
11057	5		< 0.007	
11056	5		< 0.007	
11055	5		< 0.007	
11054	5		< 0.007	
11053	5		< 0.007	
11052	4	0.044	0.056	0.068

Table 1 continued

THE CONCENTRATION OF DISSOLVED CADMIUM
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051 4	0.032	0.040	0.048
11050 4	0.032	0.040	0.048
11049 4		< 0.007	
11048 4	0.026	0.032	0.038
11047 4		< 0.007	
11046 4		< 0.007	
11045 4	0.011	0.015	0.019
11044 4		< 0.007	
11043 4	0.024	0.030	0.036
11042 4		< 0.007	
11041 4		< 0.007	
11040 4		< 0.007	
11039 4	0.048	0.060	0.072
11038 3	0.019	0.023	0.027
11037 3	0.024	0.030	0.036
11036 3		< 0.007	
11035 3		< 0.007	
11034 3		< 0.007	
11033 3		< 0.007	
11032 3		< 0.007	
11031 3		< 0.007	
11030 3		< 0.007	
11029 3		< 0.007	
11028 3		< 0.007	
11027 3		< 0.007	
11026 3		< 0.007	
11025 3		< 0.007	
11024 2		< 0.007	
11023 2		< 0.007	
11022 2		< 0.007	
11021 2	0.011	0.015	0.019
11020 2	0.028	0.034	0.040
11019 2	0.032	0.040	0.048
11018 2	0.005	0.007	0.009
11017 2	0.005	0.007	0.009
11016 2	0.012	0.016	0.020
11015 2		< 0.007	
11014 2		< 0.007	
11013 2		< 0.007	
11012 2		< 0.007	
11011 2		< 0.007	
11010 1		< 0.007	
11009 1		< 0.007	
11008 1		< 0.007	
11007 1		< 0.007	
11006 1		< 0.007	
11005 1		< 0.007	
11004 1		< 0.007	
11003 1		< 0.007	
11002 1		< 0.007	
11001 1		< 0.007	

Table 2

THE CONCENTRATION OF DISSOLVED COBALT
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER		MINIMUM	BEST VALUE	MAXIMUM
11102	8	0.000	0.049	0.060
11101	8	0.000	0.041	0.050
11100	8	0.077	0.154	0.177
11099	8	0.000	0.068	0.081
11098	8	0.000	0.066	0.079
11097	8	0.000	0.050	0.062
11096	8	0.008	0.076	0.090
11095	7	0.000	0.057	0.069
11094	7	0.079	0.156	0.179
11093	7	0.015	0.082	0.096
11092	7	0.000	0.044	0.055
11091	7	0.000	0.026	0.035
11090	7	0.000	0.025	0.034
11089	7	0.000	0.041	0.050
11088	7	0.000	0.063	0.076
11087	7	0.000	0.048	0.059
11086	7	0.000	0.049	0.060
11085	7	0.429	0.556	0.630
11084	7	0.000	0.029	0.038
11083	7	0.000	0.026	0.035
11082	7	0.000	0.031	0.040
11081	7	0.086	0.165	0.191
11080	6	0.000	0.027	0.036
11079	6	0.008	0.076	0.090
11078	6	0.000	0.056	0.068
11077	6	0.000	0.051	0.063
11076	6	0.000	0.048	0.059
11075	6	0.038	0.110	0.128
11074	6	0.000	0.018	0.025
11073	6	0.128	0.210	0.237
11072	6	0.000	0.021	0.030
11071	6	0.000	0.023	0.031
11070	6	0.000	0.023	0.031
11069	6	0.002	0.070	0.083
11068	6	0.000	0.055	0.067
11067	5	0.108	0.189	0.216
11066	5	0.000	0.054	0.066
11065	5	0.031	0.101	0.117
11064	5	0.000	0.034	0.043
11063	5	0.058	0.133	0.153
11062	5	0.000	0.025	0.034
11061	5	0.000	0.039	0.048
11060	5	0.000	0.030	0.039
11059	5	0.000	0.037	0.046
11058	5	0.000	0.026	0.035
11057	5	0.003	0.071	0.084
11056	5	0.000	0.024	0.032
11055	5	0.000	0.038	0.047
11054	5	0.000	0.034	0.043
11053	5	0.000	0.060	0.071
11052	4	0.000	0.055	0.067

Table 2 continued

THE CONCENTRATION OF DISSOLVED COBALT
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER		MINIMUM	BEST VALUE	MAXIMUM
11051	4	0.000	0.063	0.076
11050	4	0.000	0.064	0.077
11049	4	0.007	0.075	0.089
11048	4	0.000	0.059	0.070
11047	4	0.013	0.083	0.099
11046	4	0.014	0.081	0.095
11045	4	0.000	0.017	0.024
11044	4	0.000	0.034	0.043
11043	4	0.013	0.083	0.099
11042	4	0.000	0.024	0.032
11041	4	0.020	0.090	0.106
11040	4	0.000	0.026	0.035
11039	4	0.021	0.091	0.107
11038	3	0.000	0.021	0.030
11037	3	0.081	0.158	0.181
11036	3	0.000	0.014	0.021
11035	3	0.029	0.099	0.114
11034	3	0.000	0.044	0.055
11033	3	0.027	0.097	0.112
11032	3	0.000	0.060	0.071
11031	3	0.008	0.076	0.090
11030	3	0.028	0.098	0.113
11029	3	0.067	0.144	0.167
11028	3	0.000	0.021	0.030
11027	3	0.000	0.061	0.072
11026	3	0.000	0.055	0.067
11025	3	0.010	0.078	0.092
11024	2	0.000	0.036	0.045
11023	2	0.000	0.045	0.056
11022	2	0.000	0.057	0.069
11021	2	0.010	0.078	0.092
11020	2	0.000	0.044	0.055
11019	2	0.004	0.072	0.085
11018	2	0.000	0.053	0.065
11017	2	0.000	0.040	0.049
11016	2	0.000	0.016	0.025
11015	2	0.000	0.061	0.072
11014	2	0.000	0.059	0.070
11013	2	0.000	0.025	0.034
11012	2	0.000	0.049	0.060
11011	2	0.017	0.087	0.103
11010	1	0.000	0.048	0.059
11009	1	0.000	0.055	0.067
11008	1	0.000	0.042	0.053
11007	1	0.000	0.028	0.037
11006	1	0.000	0.028	0.037
11005	1	0.000	0.043	0.054
11004	1	0.000	0.044	0.055
11003	1	0.000	0.054	0.066
11002	1	0.000	0.057	0.069
11001	1	0.016	0.086	0.102

Table 3

THE CONCENTRATION OF DISSOLVED CHROMIUM
(IN NANOGRAMS/MILLILITER)

	THE RANGE REPRESENTS AT LEAST THE 95% CONFIDENCE LIMITS		
SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102 8	0.00	0.19	0.47
11101 8	0.10	0.40	0.70
11100 8	0.11	0.41	0.71
11099 8	0.00	0.21	0.49
11098 8	0.00	0.24	0.52
11097 8	0.02	0.32	0.63
11096 8	0.00	0.17	0.45
11095 7	0.03	0.31	0.60
11094 7	0.00	0.19	0.48
11093 7	0.00	0.16	0.45
11092 7	0.00	0.26	0.55
11091 7	0.00	0.14	0.41
11090 7	0.08	0.37	0.65
11089 7	0.00	0.11	0.38
11088 7	0.00	0.14	0.41
11087 7	1.20	1.68	2.15
11086 7	0.00	0.19	0.48
11085 7	0.00	0.10	0.37
11084 7	0.00	0.27	0.56
11083 7	0.00	0.13	0.40
11082 7	0.00	0.03	0.30
11081 7	0.02	0.30	0.59
11080 6	0.00	0.17	0.46
11079 6	0.00	0.03	0.30
11078 6	0.00	0.26	0.55
11077 6	0.00	0.17	0.46
11076 6	0.00	0.05	0.33
11075 6	0.04	0.32	0.61
11074 6	0.42	0.74	1.05
11073 6	0.00	0.08	0.35
11072 6	0.07	0.36	0.64
11071 6	0.00	0.05	0.33
11070 6	0.00	0.17	0.46
11069 6	0.17	0.47	0.77
11068 6	0.00	0.00	0.25
11067 5	0.00	0.01	0.28
11066 5	0.09	0.39	0.69
11065 5	0.00	0.09	0.36
11064 5	0.00	0.10	0.37
11063 5	0.00	0.02	0.29
11062 5	0.00	0.00	0.25
11061 5	0.00	0.11	0.38
11060 5	0.00	0.12	0.39
11059 5	0.00	0.25	0.53
11058 5	0.00	0.14	0.41
11057 5	0.00	0.12	0.39
11056 5	0.00	0.00	0.26
11055 5	0.00	0.02	0.29
11054 5	0.00	0.00	0.17
11053 5	0.00	0.19	0.48
11052 4	0.00	0.02	0.29

Table 3 continued

THE CONCENTRATION OF DISSOLVED CHROMIUM
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER		MINIMUM	BEST VALUE	MAXIMUM
11051	4	0.00	0.04	0.32
11050	4	0.00	0.03	0.30
11049	4	0.00	0.04	0.32
11048	4	0.00	0.00	0.22
11047	4	0.00	0.11	0.38
11046	4	0.00	0.09	0.36
11045	4	0.11	0.41	0.71
11044	4	0.00	0.00	0.29
11043	4	0.00	0.17	0.46
11042	4	0.00	0.01	0.28
11041	4	0.00	0.04	0.32
11040	4	0.00	0.16	0.45
11039	4	0.00	0.28	0.57
11038	3	0.00	0.14	0.41
11037	3	0.00	0.00	0.11
11036	3	0.00	0.11	0.38
11035	3	0.00	0.01	0.28
11034	3	0.00	0.08	0.35
11033	3	0.51	0.84	1.18
11032	3	0.00	0.12	0.39
11031	3	0.00	0.00	0.15
11030	3	0.00	0.04	0.32
11029	3	0.00	0.18	0.47
11028	3	0.00	0.14	0.41
11027	3	0.00	0.00	0.26
11026	3	0.00	0.08	0.35
11025	3	0.02	0.32	0.63
11024	2	0.00	0.01	0.28
11023	2	0.00	0.00	0.14
11022	2	0.00	0.05	0.33
11021	2	0.00	0.03	0.30
11020	2	0.00	0.08	0.35
11019	2	0.00	0.01	0.28
11018	2	0.00	0.06	0.34
11017	2	0.00	0.00	0.24
11016	2	0.00	0.00	0.27
11015	2	0.00	0.11	0.38
11014	2	0.00	0.11	0.38
11013	2	0.00	0.00	0.00
11012	2	0.00	0.00	0.11
11011	2	0.10	0.40	0.70
11010	1	0.00	0.21	0.49
11009	1	0.00	0.00	0.27
11008	1	0.00	0.14	0.43
11007	1	0.14	0.44	0.74
11006	1	0.00	0.14	0.43
11005	1	0.62	0.92	1.22
11004	1	0.00	0.00	0.11
11003	1	0.00	0.00	0.23
11002	1	0.00	0.00	0.27
11001	1	0.00	0.01	0.28

Table 4

THE CONCENTRATION OF DISSOLVED COPPER
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102 8	0.38	1.50	1.85
11101 8	0.36	1.48	1.83
11100 8	0.52	1.64	1.99
11099 8	0.20	1.29	1.62
11098 8	0.32	1.44	1.79
11097 8	0.22	1.22	1.48
11096 8	0.00	0.85	1.09
11095 7	0.00	0.53	0.65
11094 7	0.00	0.37	0.51
11093 7	0.00	0.78	1.00
11092 7	0.00	0.58	0.76
11091 7	0.00	0.43	0.59
11090 7	0.00	0.72	0.94
11089 7	0.00	0.94	1.20
11088 7	0.00	0.35	0.49
11087 7		< 0.08	
11086 7		< 0.08	
11085 7	0.00	0.05	0.15
11084 7		< 0.08	
11083 7		< 0.08	
11082 7		< 0.08	
11081 7	0.00	0.57	0.75
11080 6		< 0.08	
11079 6		< 0.08	
11078 6		< 0.08	
11077 6		< 0.08	
11076 6		< 0.08	
11075 6	0.00	0.23	0.35
11074 6	0.00	0.48	0.64
11073 6		< 0.08	
11072 6	0.00	0.45	0.61
11071 6	0.00	0.41	0.57
11070 6	0.00	0.75	0.97
11069 6	0.00	0.46	0.62
11068 6	0.00	0.57	0.75
11067 5	0.00	0.36	0.50
11066 5	0.00	0.44	0.60
11065 5	0.00	0.06	0.16
11064 5	0.00	0.55	0.73
11063 5	0.00	0.23	0.35
11062 5	0.00	0.49	0.67
11061 5	0.00	0.50	0.68
11060 5		< 0.08	
11059 5	0.00	0.08	0.18
11058 5	0.00	0.28	0.40
11057 5		< 0.08	
11056 5	0.00	0.09	0.19
11055 5	0.00	0.12	0.22
11054 5	0.00	0.13	0.23
11053 5		< 0.08	
11052 4		< 0.08	

Table 4 continued

THE CONCENTRATION OF DISSOLVED COPPER
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER		MINIMUM	BEST VALUE	MAXIMUM
11051	4		< 0.08	
11050	4		< 0.08	
11049	4		< 0.08	
11048	4		< 0.08	
11047	4		< 0.08	
11046	4		< 0.08	
11045	4		< 0.08	
11044	4	0.00	0.19	0.31
11043	4	0.00	0.18	0.28
11042	4	0.00	0.29	0.43
11041	4	0.00	0.18	0.28
11040	4	0.00	0.33	0.47
11039	4	0.00	0.15	0.25
11038	3	0.00	0.32	0.46
11037	3	0.00	0.11	0.21
11036	3	0.00	0.35	0.49
11035	3	0.00	0.08	0.18
11034	3	0.00	0.39	0.55
11033	3	0.00	0.31	0.45
11032	3	0.14	1.14	1.40
11031	3	0.00	0.35	0.49
11030	3	0.00	0.44	0.60
11029	3	0.00	0.25	0.37
11028	3	0.57	1.80	2.25
11027	3	0.00	0.22	0.34
11026	3	0.14	1.14	1.40
11025	3	0.00	0.29	0.43
11024	2	0.00	0.27	0.39
11023	2	0.00	0.20	0.32
11022	2	0.00	0.19	0.31
11021	2	0.00	0.30	0.44
11020	2	0.00	0.34	0.48
11019	2	0.00	0.17	0.27
11018	2	0.00	0.21	0.33
11017	2	0.00	0.33	0.47
11016	2	0.00	0.29	0.43
11015	2	0.00	0.27	0.39
11014	2	0.00	0.26	0.38
11013	2	0.00	0.25	0.37
11012	2	0.00	0.33	0.47
11011	2	0.00	0.32	0.46
11010	1		< 0.08	
11009	1	0.00	0.47	0.63
11008	1	0.00	0.17	0.27
11007	1	0.00	0.23	0.35
11006	1	0.32	1.44	1.79
11005	1	0.14	1.14	1.40
11004	1	0.03	1.03	1.29
11003	1	0.00	0.58	0.76
11002	1	0.00	0.25	0.37
11001	1	0.00	0.23	0.35

Table 5

THE CONCENTRATION OF DISSOLVED IRON
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102 8	0.00	2.41	3.52
11101 8	0.52	3.84	4.96
11100 8	0.00	2.41	3.52
11099 8	0.00	2.30	3.41
11098 8	0.00	1.75	2.86
11097 8	0.00	2.08	3.19
11096 8	0.00	2.63	3.74
11095 7	0.52	3.84	4.96
11094 7	0.00	1.41	2.28
11093 7	0.00	1.52	2.64
11092 7	0.00	1.30	2.42
11091 7	0.00	0.42	1.53
11090 7	0.83	4.40	5.76
11089 7	0.00	0.09	0.95
11088 7	0.00	0.42	1.53
11087 7	0.00	3.29	4.41
11086 7	0.00	0.75	1.86
11085 7	61.42	71.67	79.72
11084 7	0.00	1.19	2.06
11083 7	0.00	2.30	3.41
11082 7	0.74	4.07	5.18
11081 7	0.00	2.30	3.41
11080 6	0.00	0.53	1.40
11079 6	0.00	0.09	1.20
11078 6	0.00	0.53	1.64
11077 6	1.27	4.84	6.20
11076 6	0.00	2.52	3.63
11075 6	0.00	2.96	4.07
11074 6	0.00	0.75	1.62
11073 6	25.23	33.01	38.58
11072 6	0.00	0.75	1.62
11071 6	0.00	1.63	2.75
11070 6	0.00	1.08	1.95
11069 6	0.00	2.85	3.96
11068 6	0.00	0.97	1.84
11067 5	0.00	2.08	3.19
11066 5	0.00	3.29	4.65
11065 5	0.00	2.96	4.32
11064 5	0.00	0.97	2.09
11063 5	0.00	0.86	1.98
11062 5	0.00	1.41	2.53
11061 5	0.00	1.75	3.11
11060 5	0.00	0.20	1.31
11059 5	0.00	1.19	2.31
11058 5	0.00	0.42	1.53
11057 5	0.00	1.63	2.75
11056 5	0.00	0.86	1.98
11055 5	0.00	1.30	2.42
11054 5	0.00	1.75	2.86
11053 5	0.00	1.63	2.75
11052 4	2.04	5.61	6.97

Table 5 continued

THE CONCENTRATION OF DISSOLVED IRON
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER		MINIMUM	BEST VALUE	MAXIMUM
11051	4	0.00	1.86	2.97
11050	4	0.00	2.85	3.96
11049	4	0.38	3.95	5.32
11048	4	0.00	2.74	3.85
11047	4	0.00	1.86	2.97
11046	4	0.00	2.52	3.63
11045	4	0.00	1.30	2.42
11044	4	0.00	1.86	2.72
11043	4	0.00	2.63	3.74
11042	4	0.00	0.97	2.09
11041	4	0.00	2.52	3.63
11040	4	0.00	0.64	1.51
11039	4	0.00	2.41	3.52
11038	3	0.00	0.42	1.29
11037	3	0.00	3.18	4.30
11036	3	0.00	0.31	1.18
11035	3	11.19	16.00	18.59
11034	3	0.00	2.08	3.19
11033	3	1.16	4.73	6.09
11032	3	0.00	1.19	2.06
11031	3	0.00	2.08	3.19
11030	3	0.00	1.52	2.64
11029	3	0.00	3.18	4.30
11028	3	0.00	1.52	2.64
11027	3	0.00	0.97	1.84
11026	3	0.00	0.53	1.64
11025	3	0.00	1.08	1.95
11024	2	0.00	0.09	1.20
11023	2	0.94	4.51	5.87
11022	2	0.00	0.53	1.40
11021	2	10.00	14.56	16.91
11020	2	0.00	0.86	1.98
11019	2	0.00	0.97	2.09
11018	2	0.83	4.40	5.76
11017	2	0.00	0.09	1.20
11016	2	0.00	0.20	1.31
11015	2	0.00	0.97	2.09
11014	2	0.00	0.64	1.75
11013	2	0.00	0.09	1.20
11012	2	0.00	0.42	1.53
11011	2	0.00	1.30	2.17
11010	1	0.00	2.52	3.63
11009	1	0.00	3.29	4.41
11008	1	2.15	5.72	7.08
11007	1	0.00	1.08	2.20
11006	1	0.00	1.19	2.31
11005	1	0.00	2.96	4.07
11004	1	0.00	1.19	2.31
11003	1	0.83	4.40	5.76
11002	1	0.00	1.30	2.42
11001	1	0.00	1.97	3.08

Table 6

THE CONCENTRATION OF DISSOLVED MANGANESE
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER		MINIMUM	BEST VALUE	MAXIMUM
11102	8	1.24	1.70	2.15
11101	8	1.64	2.10	2.55
11100	8	6.62	8.20	9.77
11099	8	5.65	7.00	8.34
11098	8	2.80	3.70	4.60
11097	8	2.22	2.90	3.57
11096	8	4.95	6.30	7.64
11095	7	2.17	3.51	4.85
11094	7	6.00	8.01	10.02
11093	7	3.73	5.51	7.29
11092	7	0.00	0.61	1.27
11091	7	0.00	0.71	1.60
11090	7	0.00	0.51	1.17
11089	7	0.00	0.41	1.07
11088	7	0.00	0.71	1.60
11087	7	2.07	3.41	4.75
11086	7	0.12	1.01	1.90
11085	7	320.67	388.31	455.95
11084	7	0.00	0.81	1.70
11083	7	2.27	3.61	4.95
11082	7	2.65	4.21	5.77
11081	7	5.40	7.41	9.42
11080	6	0.69	0.90	1.10
11079	6	1.82	2.50	3.17
11078	6	2.12	2.80	3.47
11077	6	2.62	3.30	3.97
11076	6	7.85	10.10	12.34
11075	6	86.19	97.40	108.60
11074	6	0.51	0.67	0.83
11073	6	108.59	131.00	153.40
11072	6	0.52	0.68	0.84
11071	6	1.01	1.24	1.46
11070	6	0.45	0.59	0.72
11069	6	38.29	49.50	60.70
11068	6	1.54	2.00	2.45
11067	5	150.64	195.82	240.80
11066	5	0.24	0.82	1.20
11065	5	31.02	38.12	45.02
11064	5	1.67	2.72	3.57
11063	5	5.07	7.02	8.77
11062	5	1.77	2.82	3.67
11061	5	2.84	4.12	5.20
11060	5	0.04	0.60	0.96
11059	5	4.10	5.82	7.34
11058	5	0.00	0.38	0.69
11057	5	21.96	26.82	31.48
11056	5	0.16	0.74	1.12
11055	5	1.67	2.72	3.57
11054	5	1.29	2.12	2.75
11053	5	2.34	3.62	4.70
11052	4	2.78	4.04	5.30

Table 6 continued

THE CONCENTRATION OF DISSOLVED MANGANESE (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051 4	2.68	3.94	5.20
11050 4	2.38	3.64	4.90
11049 4	4.21	6.14	8.07
11048 4	3.46	4.94	6.42
11047 4	11.29	14.34	17.39
11046 4	16.60	21.44	26.28
11045 4	0.00	0.22	0.71
11044 4	0.23	1.04	1.85
11043 4	3.06	4.54	6.02
11042 4	0.00	0.27	0.76
11041 4	12.52	16.24	19.96
11040 4	0.23	0.81	1.39
11039 4	10.69	13.74	16.79
11038 3	0.70	0.91	1.11
11037 3	33.27	40.00	46.72
11036 3	0.50	0.66	0.82
11035 3	12.60	15.30	17.99
11034 3	0.52	0.68	0.84
11033 3	12.40	15.10	17.79
11032 3	0.42	0.56	0.69
11031 3	9.55	11.80	14.04
11030 3	0.68	0.89	1.09
11029 3	58.23	67.20	76.16
11028 3	0.49	0.63	0.76
11027 3	6.30	8.10	9.89
11026 3	2.80	3.70	4.60
11025 3	6.48	8.50	10.52
11024 2	0.00	0.57	1.38
11023 2	2.18	3.67	5.15
11022 2	2.58	4.07	5.55
11021 2	9.46	12.07	14.67
11020 2	1.03	2.07	3.10
11019 2	7.06	9.67	12.27
11018 2	1.60	2.87	4.13
11017 2	0.55	1.37	2.18
11016 2	0.00	0.00	0.32
11015 2	2.20	3.47	4.73
11014 2	2.00	3.27	4.53
11013 2	2.10	3.37	4.63
11012 2	1.43	2.47	3.50
11011 2	3.96	5.67	7.37
11010 1	2.37	3.64	4.90
11009 1	2.77	4.04	5.30
11008 1	0.62	1.44	2.25
11007 1	1.12	1.94	2.75
11006 1	0.90	1.94	2.97
11005 1	1.90	2.94	3.97
11004 1	1.80	2.84	3.87
11003 1	1.22	2.04	2.85
11002 1	1.02	1.84	2.65
11001 1	9.33	11.94	14.54

Table 7

THE CONCENTRATION OF DISSOLVED MOLYBDENUM
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102 8	0.87	0.97	1.07
11101 8	0.72	0.80	0.89
11100 8	0.69	0.77	0.86
11099 8	0.75	0.84	0.92
11098 8	0.59	0.65	0.71
11097 8	0.60	0.66	0.72
11096 8	0.54	0.61	0.67
11095 7	0.80	0.88	0.96
11094 7	0.58	0.64	0.70
11093 7	0.64	0.70	0.76
11092 7	1.50	1.66	1.83
11091 7	1.99	2.20	2.40
11090 7	1.49	1.65	1.82
11089 7	1.26	1.40	1.54
11088 7	1.57	1.78	1.98
11087 7	1.99	2.20	2.40
11086 7	1.78	1.99	2.19
11085 7	3.04	3.45	3.86
11084 7	1.99	2.20	2.40
11083 7	1.78	1.99	2.19
11082 7	1.89	2.09	2.30
11081 7	2.10	2.30	2.50
11080 6	1.89	2.09	2.30
11079 6	1.99	2.20	2.40
11078 6	1.99	2.20	2.40
11077 6	1.99	2.20	2.40
11076 6	2.51	2.72	2.92
11075 6	2.30	2.51	2.71
11074 6	1.99	2.20	2.40
11073 6	3.14	3.55	3.96
11072 6	1.89	2.09	2.30
11071 6	2.30	2.51	2.71
11070 6	2.41	2.61	2.82
11069 6	2.72	2.93	3.13
11068 6	2.20	2.40	2.61
11067 5	2.83	3.24	3.65
11066 5	2.30	2.51	2.71
11065 5	3.98	4.39	4.80
11064 5	2.51	2.72	2.92
11063 5	2.20	2.40	2.61
11062 5	2.20	2.40	2.61
11061 5	2.41	2.61	2.82
11060 5	2.41	2.61	2.82
11059 5	2.62	2.82	3.03
11058 5	1.99	2.20	2.40
11057 5	2.62	3.03	3.44
11056 5	1.99	2.20	2.40
11055 5	2.52	2.93	3.34
11054 5	2.52	2.93	3.34
11053 5	2.62	3.03	3.44
11052 4	2.41	2.61	2.82

Table 7 continued

THE CONCENTRATION OF DISSOLVED MOLYBDENUM
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER		MINIMUM	BEST VALUE	MAXIMUM
11051	4	2.62	3.03	3.44
11050	4	2.73	3.14	3.55
11049	4	2.30	2.51	2.71
11048	4	2.73	3.14	3.55
11047	4	2.73	3.14	3.55
11046	4	2.83	3.24	3.65
11045	4	2.51	2.72	2.92
11044	4	2.52	2.93	3.34
11043	4	3.14	3.55	3.96
11042	4	2.62	3.03	3.44
11041	4	2.94	3.35	3.76
11040	4	2.41	2.82	3.23
11039	4	3.56	3.97	4.38
11038	3	2.51	2.72	2.92
11037	3	3.56	3.97	4.38
11036	3	2.62	3.03	3.44
11035	3	3.98	4.39	4.80
11034	3	2.73	3.14	3.55
11033	3	3.98	4.39	4.80
11032	3	2.83	3.24	3.65
11031	3	3.88	4.29	4.70
11030	3	2.94	3.35	3.76
11029	3	4.51	5.12	5.74
11028	3	2.52	2.93	3.34
11027	3	2.94	3.35	3.76
11026	3	3.88	4.29	4.70
11025	3	5.03	5.65	6.26
11024	2	5.45	6.06	6.68
11023	2	5.66	6.27	6.89
11022	2	4.61	5.23	5.84
11021	2	4.61	5.02	5.43
11020	2	3.88	4.29	4.70
11019	2	4.50	4.91	5.32
11018	2	4.71	5.12	5.53
11017	2	4.19	4.60	5.01
11016	2	2.52	2.93	3.34
11015	2	5.87	6.48	7.10
11014	2	4.82	5.44	6.05
11013	2	3.56	3.97	4.38
11012	2	4.09	4.50	4.91
11011	2	5.76	6.38	6.99
11010	1	4.71	5.12	5.53
11009	1	6.60	7.42	8.24
11008	1	6.29	6.90	7.51
11007	1	7.86	8.68	9.50
11006	1	2.41	2.61	2.82
11005	1	3.56	3.97	4.38
11004	1	4.72	5.33	5.95
11003	1	5.76	6.38	6.99
11002	1	5.03	5.65	6.26
11001	1	5.24	5.85	6.47

Table 8

THE CONCENTRATION OF DISSOLVED NICKEL (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER		MINIMUM	BEST VALUE	MAXIMUM
11102	8	0.66	1.15	1.49
11101	8	0.88	1.37	1.71
11100	8	0.88	1.37	1.71
11099	8	1.02	1.58	1.99
11098	8	0.74	1.23	1.57
11097	8	0.91	1.40	1.74
11096	8	0.60	1.04	1.33
11095	7	0.15	0.92	1.30
11094	7	0.08	0.85	1.23
11093	7	0.35	1.17	1.60
11092	7	1.48	2.59	3.31
11091	7	0.76	1.65	2.15
11090	7	1.04	2.04	2.65
11089	7	0.76	1.65	2.15
11088	7	0.76	1.65	2.15
11087	7	0.85	1.85	2.46
11086	7	0.77	1.66	2.16
11085	7	0.68	1.57	2.07
11084	7	0.77	1.66	2.16
11083	7	0.95	1.95	2.56
11082	7	0.82	1.71	2.21
11081	7	0.56	1.45	1.95
11080	6	0.91	1.40	1.78
11079	6	1.04	1.53	1.91
11078	6	1.03	1.52	1.90
11077	6	0.86	1.28	1.59
11076	6	1.11	1.60	1.98
11075	6	0.68	1.10	1.41
11074	6	0.88	1.30	1.61
11073	6	0.95	1.37	1.68
11072	6	0.71	1.08	1.34
11071	6	0.57	0.94	1.20
11070	6	0.82	1.24	1.55
11069	6	0.79	1.16	1.42
11068	6	0.93	1.35	1.66
11067	5	0.87	1.28	1.59
11066	5	1.01	1.49	1.87
11065	5	0.56	0.92	1.18
11064	5	1.05	1.53	1.91
11063	5	0.77	1.13	1.39
11062	5	0.85	1.26	1.57
11061	5	0.93	1.34	1.65
11060	5	0.94	1.35	1.66
11059	5	0.70	1.06	1.32
11058	5	0.95	1.36	1.67
11057	5	0.65	1.01	1.27
11056	5	0.86	1.27	1.58
11055	5	0.71	1.07	1.33
11054	5	0.64	1.00	1.26
11053	5	0.77	1.18	1.49
11052	4	0.38	1.09	1.49

Table 8 continued

THE CONCENTRATION OF DISSOLVED NICKEL (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051 4	0.29	0.95	1.30
11050 4	0.40	1.11	1.51
11049 4	0.30	0.96	1.31
11048 4	0.47	1.25	1.72
11047 4	0.00	0.58	0.89
11046 4	0.00	0.56	0.85
11045 4	0.30	0.96	1.31
11044 4	0.62	1.40	1.87
11043 4	0.39	1.10	1.50
11042 4	0.36	1.07	1.47
11041 4	0.42	1.13	1.53
11040 4	0.46	1.17	1.57
11039 4	0.38	1.09	1.49
11038 3	0.34	1.15	1.58
11037 3	0.06	0.82	1.20
11036 3	1.31	2.30	2.91
11035 3	0.74	1.62	2.12
11034 3	1.23	2.22	2.83
11033 3	1.11	1.99	2.49
11032 3	0.31	1.12	1.55
11031 3	0.57	1.38	1.81
11030 3	0.51	1.32	1.75
11029 3	0.20	0.96	1.34
11028 3	1.05	1.93	2.43
11027 3	0.42	1.18	1.56
11026 3	0.13	0.89	1.27
11025 3	0.24	1.00	1.38
11024 2	0.62	0.90	1.13
11023 2	0.61	0.89	1.12
11022 2	0.62	0.90	1.13
11021 2	0.67	0.97	1.22
11020 2	0.85	1.15	1.40
11019 2	0.95	1.25	1.50
11018 2	0.87	1.17	1.42
11017 2	0.59	0.87	1.10
11016 2	0.70	1.00	1.25
11015 2	0.53	0.81	1.04
11014 2	0.57	0.85	1.08
11013 2	0.53	0.81	1.04
11012 2	0.66	0.94	1.17
11011 2	0.60	0.88	1.11
11010 1	0.47	0.78	0.99
11009 1	0.40	0.71	0.92
11008 1	0.55	0.88	1.11
11007 1	0.29	0.55	0.71
11006 1	0.54	0.87	1.10
11005 1	0.47	0.78	0.99
11004 1	0.48	0.81	1.04
11003 1	0.64	0.97	1.20
11002 1	0.56	0.89	1.12
11001 1	0.50	0.81	1.02

Table 9

THE CONCENTRATION OF DISSOLVED LEAD
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER		MINIMUM	BEST VALUE	MAXIMUM
11102	8	0.27	0.51	0.63
11101	8	0.00	0.00	0.12
11100	8	0.00	0.00	.
11099	8	0.00	0.08	0.20
11098	8	0.00	0.16	0.31
11097	8	0.10	0.40	0.60
11096	8	0.00	0.10	0.22
11095	7	0.03	0.33	0.52
11094	7	0.00	0.16	0.31
11093	7	0.00	0.04	0.16
11092	7	0.00	0.02	0.14
11091	7	0.00	0.00	0.12
11090	7	0.00	0.00	0.11
11089	7	0.00	0.00	0.07
11088	7	0.00	0.00	0.07
11087	7	0.00	0.21	0.36
11086	7	0.00	0.00	0.12
11085	7	0.00	0.00	0.09
11084	7	0.00	0.00	0.11
11083	7	0.00	0.00	0.11
11082	7	0.00	0.00	0.10
11081	7	0.00	0.04	0.16
11080	6	0.00	0.00	0.07
11079	6	0.00	0.00	0.04
11078	6	0.00	0.11	0.23
11077	6	0.00	0.00	0.03
11076	6	0.00	0.01	0.13
11075	6	0.00	0.00	0.05
11074	6	0.00	0.00	0.12
11073	6	0.00	0.00	0.09
11072	6	0.00	0.00	0.11
11071	6	0.00	0.05	0.17
11070	6	0.00	0.03	0.15
11069	6	0.00	0.03	0.15
11068	6	0.00	0.24	0.41
11067	5	0.08	0.38	0.57
11066	5	0.11	0.43	0.65
11065	5	0.00	0.12	0.27
11064	5	0.00	0.24	0.41
11063	5	0.00	0.13	0.28
11062	5	0.00	0.18	0.33
11061	5	0.00	0.13	0.28
11060	5	0.00	0.10	0.22
11059	5	0.00	0.08	0.20
11058	5	0.00	0.15	0.30
11057	5	0.00	0.13	0.28
11056	5	0.00	0.20	0.35
11055	5	0.00	0.13	0.28
11054	5	0.00	0.17	0.32
11053	5	0.19	0.52	0.73
11052	4	0.47	0.88	1.19

Table 9 continued

THE CONCENTRATION OF DISSOLVED LEAD
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051 4	0.00	0.00	0.11
11050 4	0.00	0.00	0.10
11049 4	0.00	0.01	0.13
11048 4	0.00	0.01	0.13
11047 4	0.00	0.05	0.17
11046 4	0.00	0.00	0.12
11045 4	0.00	0.05	0.17
11044 4	0.00	0.07	0.19
11043 4	0.00	0.03	0.15
11042 4	0.00	0.04	0.16
11041 4	0.00	0.03	0.15
11040 4	0.00	0.12	0.27
11039 4	0.00	0.22	0.39
11038 3	0.00	0.05	0.17
11037 3	0.00	0.13	0.28
11036 3	0.00	0.08	0.20
11035 3	0.00	0.05	0.17
11034 3	0.00	0.07	0.19
11033 3	0.00	0.00	0.12
11032 3	0.00	0.10	0.22
11031 3	0.00	0.06	0.18
11030 3	0.00	0.00	0.11
11029 3	0.00	0.00	0.10
11028 3	0.00	0.00	0.06
11027 3	0.00	0.04	0.16
11026 3	0.00	0.16	0.31
11025 3	0.95	1.59	2.13
11024 2	0.03	0.33	0.52
11023 2	0.00	0.20	0.35
11022 2	0.00	0.14	0.29
11021 2	0.00	0.11	0.23
11020 2	0.00	0.15	0.30
11019 2	0.00	0.06	0.18
11018 2	0.00	0.00	0.11
11017 2	0.00	0.04	0.16
11016 2	0.00	0.09	0.21
11015 2	0.00	0.13	0.25
11014 2	0.00	0.08	0.20
11013 2	0.00	0.07	0.19
11012 2	0.11	0.41	0.61
11011 2	0.00	0.18	0.33
11010 1	0.00	0.00	0.11
11009 1	0.00	0.00	0.12
11008 1	0.00	0.00	0.09
11007 1	0.00	0.00	0.11
11006 1	0.00	0.03	0.15
11005 1	0.00	0.00	0.11
11004 1	0.00	0.02	0.14
11003 1	0.00	0.08	0.20
11002 1	0.00	0.01	0.13
11001 1	0.00	0.06	0.18

Table 10

THE CONCENTRATION OF DISSOLVED SCANDIUM
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER		MINIMUM	BEST VALUE	MAXIMUM
11102	8	0.00056	0.00068	0.00080
11101	8	0.00098	0.00113	0.00128
11100	8	0.00073	0.00086	0.00100
11099	8	0.00061	0.00074	0.00087
11098	8	0.00084	0.00099	0.00115
11097	8	0.00048	0.00059	0.00071
11096	8	0.00095	0.00110	0.00126
11095	7	0.00090	0.00105	0.00121
11094	7	0.00065	0.00079	0.00092
11093	7	0.00089	0.00104	0.00119
11092	7	0.00046	0.00058	0.00070
11091	7	0.00039	0.00051	0.00063
11090	7	0.00055	0.00067	0.00079
11089	7	0.00051	0.00063	0.00075
11088	7	0.00041	0.00053	0.00065
11087	7	0.00070	0.00084	0.00097
11086	7	0.00033	0.00044	0.00054
11085	7	0.00069	0.00082	0.00096
11084	7	0.00037	0.00048	0.00060
11083	7	0.00022	0.00033	0.00043
11082	7	0.00020	0.00030	0.00041
11081	7	0.00052	0.00064	0.00076
11080	6	0.00026	0.00036	0.00047
11079	6	0.00021	0.00032	0.00042
11078	6	0.00039	0.00051	0.00063
11077	6	0.00056	0.00068	0.00080
11076	6	0.00059	0.00073	0.00086
11075	6	0.00058	0.00072	0.00085
11074	6	0.00023	0.00034	0.00045
11073	6	0.00041	0.00053	0.00065
11072	6	0.00028	0.00039	0.00049
11071	6	0.00025	0.00035	0.00046
11070	6	0.00037	0.00048	0.00060
11069	6	0.00026	0.00036	0.00047
11068	6	0.00022	0.00033	0.00043
11067	5	0.00015	0.00025	0.00036
11066	5	0.00023	0.00034	0.00045
11065	5	0.00020	0.00030	0.00041
11064	5	0.00049	0.00061	0.00072
11063	5	0.00044	0.00056	0.00068
11062	5	0.00058	0.00072	0.00085
11061	5	0.00076	0.00090	0.00103
11060	5	0.00017	0.00028	0.00039
11059	5	0.00021	0.00032	0.00042
11058	5	0.00012	0.00023	0.00034
11057	5	0.00027	0.00038	0.00048
11056	5	0.00031	0.00041	0.00052
11055	5	0.00034	0.00046	0.00058
11054	5	0.00046	0.00058	0.00070
11053	5	0.00048	0.00059	0.00071
11052	4	0.00048	0.00059	0.00071

Table 10 continued

THE CONCENTRATION OF DISSOLVED SCANDIUM
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051 4	0.00031	0.00041	0.00052
11050 4	0.00070	0.00084	0.00097
11049 4	0.00033	0.00044	0.00054
11048 4	0.00029	0.00040	0.00051
11047 4	0.00035	0.00047	0.00059
11046 4	0.00034	0.00046	0.00058
11045 4	0.00025	0.00035	0.00046
11044 4	0.00021	0.00032	0.00042
11043 4	0.00056	0.00068	0.00080
11042 4	0.00017	0.00028	0.00039
11041 4	0.00050	0.00062	0.00074
11040 4	0.00020	0.00032	0.00043
11039 4	0.00038	0.00050	0.00062
11038 3	0.00032	0.00042	0.00053
11037 3	0.00018	0.00030	0.00042
11036 3	0.00018	0.00029	0.00040
11035 3	0.00214	0.00240	0.00266
11034 3	0.00017	0.00028	0.00039
11033 3	0.00081	0.00096	0.00111
11032 3	0.00031	0.00041	0.00052
11031 3	0.00035	0.00047	0.00059
11030 3	0.00026	0.00036	0.00047
11029 3	0.00045	0.00057	0.00069
11028 3	0.00033	0.00045	0.00057
11027 3	0.00032	0.00044	0.00056
11026 3	0.00021	0.00032	0.00042
11025 3	0.00033	0.00045	0.00057
11024 2	0.00032	0.00042	0.00053
11023 2	0.00089	0.00104	0.00119
11022 2	0.00028	0.00039	0.00049
11021 2	0.00028	0.00039	0.00049
11020 2	0.00034	0.00046	0.00058
11019 2	0.00037	0.00048	0.00060
11018 2	0.00039	0.00051	0.00063
11017 2	0.00031	0.00041	0.00052
11016 2	0.00021	0.00032	0.00042
11015 2	0.00025	0.00035	0.00046
11014 2	0.00029	0.00040	0.00051
11013 2	0.00012	0.00023	0.00034
11012 2	0.00022	0.00033	0.00043
11011 2	0.00103	0.00120	0.00137
11010 1	0.00035	0.00047	0.00059
11009 1	0.00033	0.00044	0.00054
11008 1	0.00101	0.00116	0.00132
11007 1	0.00083	0.00098	0.00113
11006 1	0.00068	0.00081	0.00095
11005 1	0.00059	0.00073	0.00086
11004 1	0.00069	0.00082	0.00096
11003 1	0.00044	0.00056	0.00068
11002 1	0.00034	0.00045	0.00055
11001 1	0.00037	0.00048	0.00060

Table 11

THE CONCENTRATION OF DISSOLVED TIN (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102 8	0.19	0.31	0.43
11101 8	1.44	1.61	1.78
11100 8		< 0.40	
11099 8		< 0.40	
11098 8	0.26	0.50	0.74
11097 8		< 0.40	
11096 8		< 0.40	
11095 7		< 0.50	
11094 7		< 0.40	
11093 7		< 0.40	
11092 7		< 0.50	
11091 7		< 0.20	
11090 7		< 0.30	
11089 7		< 0.30	
11088 7		< 0.60	
11087 7		< 0.60	
11086 7		< 0.50	
11085 7		< 0.50	
11084 7		< 0.90	
11083 7		< 0.50	
11082 7		< 0.50	
11081 7		< 0.60	
11080 6	0.13	0.37	0.61
11079 6		< 0.40	
11078 6		< 0.50	
11077 6	0.74	1.10	1.46
11076 6	0.68	0.97	1.26
11075 6	0.87	1.35	1.83
11074 6		< 0.50	
11073 6		< 0.50	
11072 6		< 0.40	
11071 6		< 0.50	
11070 6		< 0.40	
11069 6		< 0.50	
11068 6		< 0.50	
11067 5		< 0.60	
11066 5		< 0.50	
11065 5		< 0.50	
11064 5		< 0.50	
11063 5		< 0.60	
11062 5		< 0.50	
11061 5		< 0.50	
11060 5		< 0.50	
11059 5		< 0.50	
11058 5		< 0.50	
11057 5		< 0.50	
11056 5		< 0.50	
11055 5		< 0.50	
11054 5		< 0.50	
11053 5		< 0.50	
11052 4		< 0.40	

Table 11 continued

THE CONCENTRATION OF DISSOLVED TIN
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051 4		< 0.40	
11050 4		< 0.60	
11049 4		< 0.50	
11048 4		< 0.50	
11047 4		< 0.50	
11046 4		< 0.50	
11045 4		< 0.50	
11044 4		< 0.40	
11043 4		< 0.60	
11042 4		< 0.50	
11041 4		< 0.50	
11040 4		< 0.50	
11039 4		< 0.40	
11038 3		< 0.50	
11037 3		< 0.60	
11036 3		< 0.60	
11035 3		< 0.60	
11034 3		< 0.70	
11033 3		< 0.60	
11032 3		< 0.50	
11031 3		< 0.60	
11030 3		< 0.50	
11029 3		< 0.50	
11028 3		< 0.50	
11027 3		< 0.50	
11026 3		< 0.60	
11025 3		< 0.60	
11024 2		< 0.60	
11023 2	0.14	0.86	1.58
11022 2		< 0.60	
11021 2		< 0.60	
11020 2		< 0.60	
11019 2		< 0.60	
11018 2		< 0.60	
11017 2		< 0.40	
11016 2	0.40	0.64	0.88
11015 2		< 0.40	
11014 2		< 0.60	
11013 2		< 0.40	
11012 2		< 0.40	
11011 2		< 0.50	
11010 1		< 0.40	
11009 1		< 0.60	
11008 1		< 0.70	
11007 1		< 0.60	
11006 1		< 0.50	
11005 1		< 0.60	
11004 1		< 0.50	
11003 1		< 0.30	
11002 1		< 0.40	
11001 1		< 0.40	

Table 12

THE CONCENTRATION OF DISSOLVED THORIUM (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102 8	0.00000	0.00137	0.00259
11101 8	0.00000	0.00571	0.00694
11100 8	0.00000	0.00199	0.00346
11099 8	0.00000	0.00124	0.00223
11098 8	0.00000	0.00137	0.00235
11097 8		< 0.00100	
11096 8	0.00000	0.00112	0.00210
11095 7	0.00000	0.00075	0.00222
11094 7	0.00000	0.00099	0.00246
11093 7	0.00000	0.00099	0.00246
11092 7	0.00000	0.00124	0.00247
11091 7	0.00000	0.00037	0.00136
11090 7	0.00000	0.00025	0.00123
11089 7	0.00000	0.00037	0.00136
11088 7		< 0.00200	
11087 7		< 0.00200	
11086 7		< 0.00100	
11085 7		< 0.00200	
11084 7		< 0.00100	
11083 7		< 0.00080	
11082 7	0.00000	0.00050	0.00172
11081 7	0.00000	0.00087	0.00185
11080 6		< 0.00080	
11079 6		< 0.00090	
11078 6		< 0.00090	
11077 6	0.00000	0.00161	0.00260
11076 6	0.00000	0.00161	0.00260
11075 6	0.00000	0.00248	0.00347
11074 6		< 0.00090	
11073 6		< 0.00090	
11072 6		< 0.00080	
11071 6		< 0.00090	
11070 6		< 0.00090	
11069 6		< 0.00090	
11068 6		< 0.00090	
11067 5	0.00000	0.00112	0.00259
11066 5	0.00000	0.00112	0.00259
11065 5		< 0.00100	
11064 5		< 0.00100	
11063 5		< 0.00100	
11062 5		< 0.00100	
11061 5		< 0.00100	
11060 5		< 0.00100	
11059 5		< 0.00100	
11058 5		< 0.00100	
11057 5		< 0.00100	
11056 5		< 0.00100	
11055 5		< 0.00100	
11054 5		< 0.00090	
11053 5		< 0.00090	
11052 4		< 0.00070	

Table 12 continued

THE CONCENTRATION OF DISSOLVED THORIUM (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER		MINIMUM	BEST VALUE	MAXIMUM
11051	4	0.00000	0.00037	0.00136
11050	4	0.00000	0.00075	0.00197
11049	4		< 0.00090	
11048	4		< 0.00070	
11047	4		< 0.00080	
11046	4		< 0.00090	
11045	4	0.00000	0.00050	0.00148
11044	4	0.00000	0.00037	0.00136
11043	4		< 0.00090	
11042	4		< 0.00070	
11041	4		< 0.00080	
11040	4		< 0.00070	
11039	4		< 0.00060	
11038	3		< 0.00080	
11037	3		< 0.00080	
11036	3	0.00000	0.00174	0.00272
11035	3	0.00000	0.00385	0.00508
11034	3	0.00000	0.00161	0.00260
11033	3	0.00000	0.00211	0.00309
11032	3	0.00000	0.00211	0.00334
11031	3	0.00000	0.00137	0.00235
11030	3		< 0.00060	
11029	3	0.00000	0.00025	0.00123
11028	3		< 0.00070	
11027	3		< 0.00060	
11026	3		< 0.00090	
11025	3		< 0.00080	
11024	2		< 0.00100	
11023	2	0.00000	0.00112	0.00234
11022	2		< 0.00100	
11021	2		< 0.00100	
11020	2	0.00000	0.00075	0.00197
11019	2		< 0.00100	
11018	2		< 0.00100	
11017	2	0.00000	0.00025	0.00123
11016	2	0.00000	0.00075	0.00173
11015	2		< 0.00070	
11014	2		< 0.00070	
11013	2		< 0.00050	
11012	2		< 0.00060	
11011	2		< 0.00060	
11010	1	0.00000	0.00025	0.00123
11009	1		< 0.00090	
11008	1		< 0.00100	
11007	1		< 0.00100	
11006	1		< 0.00070	
11005	1		< 0.00090	
11004	1		< 0.00070	
11003	1	0.00000	0.00011	0.00092
11002	1	0.00000	0.00006	0.00088
11001	1	0.00000	0.00050	0.00148

Table 13

THE CONCENTRATION OF DISSOLVED URANIUM
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102 8	0.124	0.138	0.152
11101 8	0.117	0.130	0.142
11100 8	0.175	0.195	0.216
11099 8	0.146	0.163	0.179
11098 8	0.190	0.210	0.230
11097 8	0.161	0.179	0.197
11096 8	0.161	0.179	0.197
11095 7	0.154	0.170	0.186
11094 7	0.168	0.186	0.204
11093 7	0.158	0.176	0.194
11092 7	0.258	0.278	0.298
11091 7	0.330	0.370	0.411
11090 7	0.237	0.257	0.277
11089 7	0.237	0.257	0.277
11088 7	0.464	0.504	0.544
11087 7	0.464	0.525	0.585
11086 7	0.464	0.504	0.544
11085 7	0.928	1.028	1.129
11084 7	0.474	0.535	0.595
11083 7	0.443	0.483	0.524
11082 7	0.526	0.586	0.647
11081 7	0.515	0.576	0.636
11080 6	0.536	0.597	0.657
11079 6	0.515	0.576	0.636
11078 6	0.454	0.514	0.575
11077 6	0.485	0.545	0.606
11076 6	0.670	0.751	0.831
11075 6	0.711	0.792	0.873
11074 6	0.577	0.638	0.698
11073 6	1.103	1.224	1.345
11072 6	0.557	0.617	0.678
11071 6	0.598	0.658	0.719
11070 6	0.639	0.699	0.760
11069 6	0.876	0.977	1.078
11068 6	0.639	0.720	0.801
11067 5	0.742	0.823	0.903
11066 5	0.649	0.710	0.770
11065 5	1.247	1.388	1.530
11064 5	0.794	0.874	0.955
11063 5	0.773	0.854	0.934
11062 5	0.577	0.638	0.698
11061 5	0.650	0.730	0.811
11060 5	0.670	0.751	0.831
11059 5	0.814	0.895	0.975
11058 5	0.598	0.658	0.719
11057 5	0.989	1.090	1.191
11056 5	0.546	0.607	0.667
11055 5	0.763	0.843	0.924
11054 5	0.691	0.771	0.852
11053 5	0.732	0.813	0.893
11052 4	0.824	0.905	0.986

Table 13 continued

THE CONCENTRATION OF DISSOLVED URANIUM
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051 4	0.938	1.039	1.140
11050 4	0.989	1.090	1.191
11049 4	0.814	0.895	0.975
11048 4	1.010	1.111	1.212
11047 4	0.989	1.090	1.191
11046 4	1.000	1.100	1.201
11045 4	0.742	0.823	0.903
11044 4	0.608	0.669	0.729
11043 4	1.052	1.172	1.293
11042 4	0.866	0.967	1.068
11041 4	1.371	1.512	1.653
11040 4	0.917	1.018	1.119
11039 4	1.443	1.604	1.766
11038 3	0.691	0.771	0.852
11037 3	1.165	1.286	1.407
11036 3	0.814	0.895	0.975
11035 3	1.217	1.358	1.499
11034 3	0.845	0.946	1.047
11033 3	1.237	1.378	1.519
11032 3	0.856	0.957	1.057
11031 3	1.144	1.265	1.386
11030 3	0.887	0.987	1.088
11029 3	1.412	1.574	1.735
11028 3	0.660	0.741	0.821
11027 3	0.804	0.885	0.965
11026 3	1.185	1.306	1.427
11025 3	1.515	1.676	1.838
11024 2	1.371	1.512	1.653
11023 2	1.484	1.646	1.807
11022 2	1.134	1.255	1.376
11021 2	1.154	1.275	1.396
11020 2	1.000	1.100	1.201
11019 2	1.154	1.275	1.396
11018 2	1.154	1.275	1.396
11017 2	1.072	1.193	1.314
11016 2	0.752	0.833	0.914
11015 2	1.402	1.563	1.725
11014 2	1.505	1.666	1.827
11013 2	0.608	0.669	0.729
11012 2	1.258	1.399	1.540
11011 2	1.958	2.160	2.361
11010 1	1.258	1.399	1.540
11009 1	1.525	1.687	1.848
11008 1	1.773	1.975	2.176
11007 1	2.370	2.571	2.773
11006 1	0.567	0.627	0.688
11005 1	0.969	1.070	1.170
11004 1	1.196	1.316	1.437
11003 1	1.464	1.625	1.786
11002 1	1.258	1.399	1.540
11001 1	1.350	1.491	1.632

Table 14

THE CONCENTRATION OF DISSOLVED ZINC
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102 8	0.00	0.00	0.91
11101 8	0.00	0.00	0.71
11100 8	0.00	1.39	3.94
11099 8	0.00	0.67	3.22
11098 8	0.00	0.00	0.42
11097 8	0.00	0.00	1.55
11096 8	0.00	0.00	1.86
11095 7	0.00	0.69	2.32
11094 7	4.14	8.09	10.64
11093 7	1.80	5.52	7.84
11092 7	0.00	1.92	3.78
11091 7	0.00	2.44	4.30
11090 7	0.00	0.00	1.47
11089 7	0.00	0.69	2.32
11088 7	0.00	2.64	4.50
11087 7	0.00	2.64	4.50
11086 7	0.00	0.38	2.01
11085 7	0.00	1.10	2.73
11084 7	0.00	0.00	0.47
11083 7	0.00	0.00	1.42
11082 7	0.00	0.38	2.01
11081 7	0.00	1.82	3.68
11080 6	0.00	0.25	1.77
11079 6	0.00	0.00	1.06
11078 6	0.00	1.06	2.61
11077 6	0.00	0.65	2.19
11076 6	0.19	3.53	5.54
11075 6	0.00	0.85	2.40
11074 6	0.00	1.06	2.61
11073 6	0.00	0.00	1.01
11072 6	0.00	0.00	0.64
11071 6	0.00	0.00	1.04
11070 6	0.00	0.00	0.65
11069 6	0.00	0.85	2.40
11068 6	0.00	0.36	1.91
11067 5	0.00	2.27	3.80
11066 5	0.00	0.33	1.56
11065 5	0.00	0.00	0.88
11064 5	2.31	5.15	6.91
11063 5	0.00	0.00	1.17
11062 5	0.00	0.00	1.16
11061 5	0.00	0.07	1.28
11060 5	1.69	4.54	6.30
11059 5	0.00	0.00	1.00
11058 5	0.00	0.38	1.61
11057 5	0.00	0.00	1.02
11056 5	0.00	0.06	1.27
11055 5	0.00	0.00	1.02
11054 5	1.39	4.23	5.99
11053 5	0.00	0.88	2.18
11052 4	0.00	0.00	1.17

Table 14 continued

THE CONCENTRATION OF DISSOLVED ZINC
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051 4	0.00	0.00	0.79
11050 4	2.86	6.06	8.11
11049 4	0.00	0.00	1.27
11048 4	0.00	0.13	1.43
11047 4	0.00	0.00	1.01
11046 4	0.00	0.31	1.62
11045 4	0.00	0.00	1.10
11044 4	0.00	1.94	3.54
11043 4	0.00	0.20	1.49
11042 4	0.00	0.00	0.91
11041 4	0.00	0.00	1.12
11040 4	0.00	0.21	1.50
11039 4	0.00	1.02	2.38
11038 3	0.00	0.81	1.82
11037 3	0.00	0.14	1.08
11036 3	0.88	3.19	4.47
11035 3	0.00	0.42	1.38
11034 3	7.87	11.11	13.31
11033 3	0.00	0.75	1.76
11032 3	5.35	8.13	9.87
11031 3	0.00	0.00	0.87
11030 3	0.00	0.43	1.39
11029 3	0.00	1.09	2.12
11028 3	0.00	0.98	2.01
11027 3	0.00	0.97	2.00
11026 3	0.05	2.37	3.65
11025 3	0.00	0.37	1.33
11024 2	0.00	1.25	2.39
11023 2	0.00	0.06	1.08
11022 2	0.00	0.75	1.84
11021 2	0.00	0.64	1.73
11020 2	0.00	1.36	2.49
11019 2	0.00	1.15	2.29
11018 2	0.00	2.28	3.65
11017 2	0.00	0.53	1.60
11016 2	0.00	0.00	0.78
11015 2	0.00	0.00	0.74
11014 2	0.00	0.43	1.50
11013 2	0.00	0.00	0.77
11012 2	0.00	0.00	0.89
11011 2	0.00	0.22	1.24
11010 1	0.00	0.56	1.27
11009 1	0.00	0.23	0.89
11008 1	0.00	0.31	0.98
11007 1	0.00	0.14	0.81
11006 1	0.00	1.43	2.24
11005 1	0.00	1.36	2.14
11004 1	0.47	2.30	3.11
11003 1	0.00	0.92	1.65
11002 1	5.43	7.96	9.46
11001 1	0.00	0.41	1.10

Table 15

THE CONCENTRATION OF PARTICULATE CADMIUM
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102	0.016	0.024	0.032
11101	0.075	0.093	0.111
11100	0.002	0.004	0.006
11099	0.011	0.015	0.019
11098	0.030	0.040	0.050
11097	0.050	0.066	0.082
11096	0.013	0.021	0.029
11095	0.016	0.024	0.032
11094	0.045	0.059	0.073
11093	0.081	0.099	0.117
11092	0.011	0.017	0.023
11091	0.012	0.018	0.024
11090	0.001	0.003	0.005
11089	0.005	0.009	0.013
11088	0.002	0.006	0.010
11087	0.006	0.010	0.014
11086	0.000	0.001	0.003
11085		< 0.001	
11084		< 0.001	
11083	0.001	0.003	0.005
11082	0.001	0.003	0.005
11081		< 0.001	
11080	0.006	0.010	0.014
11079	0.002	0.004	0.006
11078	0.007	0.015	0.023
11077	0.003	0.007	0.011
11076	0.000	0.002	0.004
11075		< 0.001	
11074	0.004	0.008	0.012
11073	0.003	0.005	0.007
11072	0.009	0.017	0.025
11071	0.009	0.017	0.025
11070	0.000	0.002	0.004
11069	0.000	0.002	0.004
11068	0.000	0.002	0.004
11067	0.003	0.007	0.011
11066	0.002	0.004	0.006
11065		< 0.001	
11064		< 0.001	
11063	0.004	0.008	0.012
11062		< 0.001	
11061	0.008	0.012	0.016
11060		< 0.001	
11059		< 0.001	
11058	0.000	0.001	0.003
11057		< 0.001	
11056		< 0.001	
11055		< 0.001	
11054		< 0.001	
11053		< 0.001	
11052		< 0.001	

Table 15 continued

THE CONCENTRATION OF PARTICULATE CADMIUM
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051		< 0.001	
11050		< 0.001	
11049		< 0.001	
11048	0.090	0.110	0.130
11047	0.014	0.020	0.026
11046	0.001	0.003	0.005
11045	0.017	0.023	0.029
11044		< 0.001	
11043	0.005	0.007	0.009
11042		< 0.001	
11041		< 0.001	
11040		< 0.001	
11039		< 0.001	
11038		< 0.001	
11037		< 0.001	
11036	0.018	0.022	0.026
11035		< 0.001	
11034		< 0.001	
11033		< 0.001	
11032		< 0.001	
11031		< 0.001	
11030		< 0.001	
11029		< 0.001	
11028		< 0.001	
11027		< 0.001	
11026		< 0.001	
11025		< 0.001	
11024		< 0.001	
11023		< 0.001	
11022		< 0.001	
11021	0.040	0.060	0.080
11020	0.000	0.001	0.003
11019	0.005	0.011	0.017
11018		< 0.001	
11017	0.000	0.001	0.003
11016		< 0.001	
11015		< 0.001	
11014		< 0.001	
11013		< 0.001	
11012		< 0.001	
11011	0.000	0.002	0.004
11010		< 0.001	
11009	0.000	0.002	0.004
11008		< 0.001	
11007		< 0.001	
11006		< 0.001	
11005	0.001	0.003	0.005
11004		< 0.001	
11003	0.002	0.004	0.006
11002		< 0.001	
11001	0.003	0.005	0.007

Table 16

THE CONCENTRATION OF PARTICULATE CERIUM
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102	3.608	4.011	4.414
11101	3.814	4.217	4.620
11100	1.165	1.286	1.407
11099	1.227	1.368	1.509
11098	2.370	2.571	2.773
11097	2.682	3.085	3.489
11096	3.814	4.217	4.620
11095	3.711	4.114	4.517
11094	4.431	4.834	5.237
11093	4.328	4.731	5.134
11092	1.402	1.563	1.725
11091	2.575	2.777	2.978
11090	0.783	0.864	0.945
11089	0.804	0.884	0.965
11088	0.474	0.535	0.595
11087	1.031	1.152	1.273
11086	0.092	0.102	0.112
11085	0.127	0.141	0.155
11084	0.127	0.141	0.155
11083	0.144	0.160	0.177
11082	0.072	0.080	0.088
11081	0.157	0.175	0.193
11080	0.057	0.063	0.069
11079	0.057	0.065	0.073
11078	0.299	0.339	0.380
11077	0.309	0.350	0.390
11076	0.123	0.137	0.151
11075	0.142	0.158	0.175
11074	0.065	0.071	0.077
11073	0.114	0.127	0.139
11072	0.186	0.206	0.226
11071	0.278	0.298	0.318
11070	0.061	0.069	0.077
11069	0.137	0.151	0.165
11068	0.154	0.170	0.186
11067	0.402	0.442	0.483
11066	0.044	0.057	0.069
11065	0.155	0.175	0.195
11064	0.227	0.267	0.308
11063	0.618	0.679	0.739
11062	1.814	2.016	2.217
11061	0.680	0.761	0.842
11060	0.033	0.037	0.041
11059	0.037	0.043	0.049
11058	0.038	0.044	0.050
11057	0.175	0.195	0.216
11056	0.081	0.089	0.098
11055	0.237	0.257	0.277
11054	0.392	0.432	0.472
11053	0.680	0.761	0.842
11052	0.289	0.329	0.369

Table 16 continued

THE CONCENTRATION OF PARTICULATE CERIUM
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051	0.279	0.319	0.359
11050	0.485	0.545	0.606
11049	0.454	0.514	0.575
11048	0.258	0.298	0.339
11047	0.794	0.874	0.955
11046	0.039	0.043	0.047
11045	0.969	1.070	1.170
11044	0.279	0.319	0.359
11043	0.783	0.864	0.945
11042	0.035	0.039	0.043
11041	0.268	0.309	0.349
11040	0.030	0.034	0.038
11039	0.938	1.039	1.140
11038	0.044	0.052	0.061
11037	0.248	0.288	0.328
11036		< 0.020	
11035	0.165	0.185	0.205
11034	0.019	0.023	0.027
11033	0.186	0.206	0.226
11032	0.034	0.040	0.046
11031	0.081	0.094	0.106
11030	0.144	0.165	0.185
11029	0.763	0.843	0.924
11028	0.124	0.144	0.164
11027	0.453	0.494	0.534
11026	0.144	0.165	0.185
11025	0.279	0.319	0.359
11024	0.085	0.095	0.105
11023	0.453	0.494	0.534
11022	0.207	0.247	0.287
11021	0.928	1.028	1.129
11020	0.139	0.153	0.167
11019	0.577	0.638	0.698
11018	0.794	0.874	0.955
11017	0.701	0.782	0.862
11016	0.027	0.039	0.051
11015	0.402	0.442	0.483
11014	0.093	0.113	0.133
11013	0.216	0.237	0.257
11012	0.206	0.226	0.246
11011	1.010	1.111	1.212
11010	0.105	0.117	0.129
11009	0.237	0.278	0.318
11008	0.155	0.175	0.195
11007	0.247	0.267	0.288
11006	1.629	1.810	1.992
11005	5.566	6.171	6.775
11004	0.825	0.926	1.026
11003	0.526	0.586	0.647
11002	0.144	0.165	0.185
11001	0.433	0.473	0.513

Table 17

THE CONCENTRATION OF PARTICULATE COBALT
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102	1.134	1.255	1.376
11101	1.175	1.296	1.417
11100	0.567	0.627	0.688
11099	0.608	0.668	0.729
11098	1.051	1.172	1.293
11097	1.268	1.409	1.550
11096	1.206	1.347	1.488
11095	1.165	1.286	1.407
11094	2.164	2.365	2.567
11093	2.164	2.365	2.567
11092	0.474	0.535	0.595
11091	1.103	1.224	1.345
11090	0.340	0.381	0.421
11089	0.350	0.391	0.431
11088	0.175	0.193	0.211
11087	0.402	0.442	0.483
11086	0.048	0.055	0.061
11085	0.027	0.031	0.035
11084	0.053	0.059	0.065
11083	0.057	0.063	0.069
11082	0.040	0.044	0.048
11081	0.068	0.076	0.084
11080	0.030	0.034	0.038
11079	0.034	0.038	0.042
11078	0.065	0.071	0.077
11077	0.064	0.072	0.080
11076	0.037	0.043	0.049
11075	0.053	0.059	0.065
11074	0.029	0.033	0.037
11073	0.015	0.017	0.019
11072	0.044	0.050	0.056
11071	0.064	0.072	0.080
11070	0.026	0.030	0.034
11069	0.040	0.044	0.048
11068	0.036	0.042	0.048
11067	0.092	0.102	0.112
11066	0.013	0.023	0.033
11065	0.027	0.037	0.047
11064	0.013	0.029	0.045
11063	0.054	0.066	0.078
11062	0.289	0.329	0.369
11061	0.117	0.130	0.142
11060	0.019	0.023	0.027
11059	0.026	0.030	0.034
11058	0.018	0.022	0.026
11057	0.035	0.039	0.043
11056	0.037	0.045	0.053
11055	0.059	0.065	0.071
11054	0.064	0.072	0.080
11053	0.109	0.121	0.133
11052	0.039	0.047	0.055

Table 17 continued

THE CONCENTRATION OF PARTICULATE COBALT
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051	0.053	0.059	0.065
11050	0.074	0.084	0.094
11049	0.081	0.092	0.102
11048	0.057	0.063	0.069
11047	0.128	0.142	0.156
11046	0.022	0.026	0.030
11045	0.164	0.182	0.200
11044	0.063	0.071	0.079
11043	0.206	0.226	0.246
11042	0.028	0.032	0.036
11041	0.044	0.050	0.056
11040	0.033	0.037	0.041
11039	0.156	0.172	0.188
11038	0.036	0.042	0.048
11037	0.043	0.049	0.055
11036	0.028	0.040	0.052
11035	0.029	0.035	0.041
11034	0.019	0.021	0.023
11033	0.040	0.046	0.052
11032	0.023	0.029	0.035
11031	0.064	0.074	0.084
11030	0.040	0.050	0.060
11029	0.112	0.127	0.141
11028	0.054	0.062	0.070
11027	0.100	0.112	0.124
11026	0.035	0.041	0.047
11025	0.043	0.051	0.059
11024	0.025	0.031	0.037
11023	0.093	0.107	0.121
11022	0.047	0.067	0.087
11021	0.148	0.165	0.181
11020	0.036	0.042	0.048
11019	0.106	0.118	0.130
11018	0.165	0.183	0.201
11017	0.163	0.181	0.199
11016	0.026	0.034	0.042
11015	0.062	0.072	0.082
11014	0.041	0.053	0.066
11013	0.051	0.057	0.063
11012	0.049	0.059	0.069
11011	0.148	0.165	0.181
11010	0.023	0.029	0.035
11009	0.057	0.069	0.081
11008	0.031	0.035	0.039
11007	0.047	0.053	0.060
11006	0.258	0.298	0.339
11005	0.948	1.049	1.150
11004	0.155	0.171	0.187
11003	0.097	0.109	0.121
11002	0.039	0.051	0.064
11001	0.072	0.080	0.088

Table 18

THE CONCENTRATION OF PARTICULATE CHROMIUM (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102	3.58	4.49	5.16
11101	3.45	4.60	5.49
11100	0.82	1.27	1.49
11099	0.86	1.31	1.53
11098	2.01	2.62	3.00
11097	2.30	3.14	3.74
11096	3.76	4.91	5.80
11095	3.86	5.01	5.91
11094	3.63	4.47	5.08
11093	3.63	4.47	5.08
11092	1.52	2.44	3.10
11091	2.55	3.47	4.13
11090	0.47	0.99	1.27
11089	0.43	0.95	1.23
11088	0.17	0.67	0.93
11087	0.85	1.44	1.79
11086	0.00	0.14	0.36
11085	0.00	0.13	0.35
11084	0.00	0.23	0.44
11083	0.00	0.22	0.43
11082	0.00	0.16	0.44
11081	0.00	0.34	0.55
11080	0.00	0.09	0.68
11079	0.00	0.14	0.73
11078	0.00	0.37	1.14
11077	0.00	0.22	0.80
11076	0.00	0.09	0.68
11075	0.00	0.59	1.22
11074	0.00	0.16	0.75
11073	0.00	0.00	0.55
11072	0.00	0.27	0.85
11071	0.00	0.36	0.97
11070	0.00	0.00	0.53
11069	0.00	0.25	0.83
11068	0.00	0.02	0.58
11067	0.00	0.44	1.05
11066	0.00	0.00	0.52
11065	0.00	0.11	0.70
11064	0.00	0.15	0.74
11063	0.00	0.44	1.05
11062	0.48	1.71	2.70
11061	0.00	0.00	0.54
11060	0.00	0.00	0.34
11059	0.00	0.00	0.37
11058	0.00	0.13	0.72
11057	0.00	0.08	0.67
11056	0.00	0.01	0.57
11055	0.00	0.38	0.99
11054	0.00	0.22	0.80
11053	0.00	0.52	1.16
11052	0.00	0.39	1.00

Table 18 continued

THE CONCENTRATION OF PARTICULATE CHROMIUM
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051	0.00	0.14	0.73
11050	0.00	0.07	0.66
11049	0.00	0.22	0.80
11048	0.00	0.00	0.46
11047	0.00	0.19	1.00
11046	0.00	0.00	0.15
11045	0.00	0.00	0.71
11044	0.00	0.00	0.34
11043	0.00	0.30	1.11
11042	0.00	0.00	0.35
11041	0.00	0.00	0.25
11040	0.00	0.00	0.43
11039	0.73	1.71	2.45
11038	0.00	0.00	0.19
11037	0.00	0.00	0.44
11036	0.00	0.00	0.15
11035	0.00	0.00	0.14
11034	0.00	0.00	0.49
11033	0.00	0.17	0.76
11032	0.00	0.19	1.00
11031	0.00	0.16	0.75
11030	0.00	0.69	1.34
11029	0.06	0.97	1.64
11028	0.00	0.30	0.91
11027	0.00	0.14	1.00
11026	0.00	0.00	0.02
11025	0.00	0.74	1.40
11024	0.00	0.22	0.80
11023	0.00	0.60	1.23
11022	0.00	0.15	0.74
11021	0.47	1.42	2.14
11020	0.00	0.47	1.31
11019	0.00	0.38	1.21
11018	0.00	0.85	1.73
11017	0.00	0.86	1.74
11016	0.00	0.06	0.62
11015	0.00	0.33	0.94
11014	0.00	0.24	0.59
11013	0.00	0.14	0.73
11012	0.00	0.42	1.03
11011	0.00	0.47	1.08
11010	0.00	0.00	0.46
11009	0.00	0.58	1.21
11008	0.00	0.17	0.50
11007	0.00	0.22	0.57
11006	0.51	1.46	2.18
11005	3.61	5.31	6.76
11004	0.00	0.45	1.29
11003	0.00	0.60	1.45
11002	0.00	0.01	0.57
11001	0.00	0.50	1.14

Table 19

THE CONCENTRATION OF PARTICULATE COPPER
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102	0.19	1.02	1.76
11101	0.39	1.22	1.96
11100	0.43	0.87	1.24
11099	0.33	0.77	1.14
11098	0.59	1.34	2.02
11097	0.77	1.74	2.64
11096	0.37	1.42	2.38
11095	0.37	1.42	2.38
11094	0.92	2.34	3.69
11093	1.92	3.34	4.69
11092	0.00	0.62	1.36
11091	0.19	1.02	1.76
11090	0.00	0.32	0.73
11089	0.00	0.27	0.68
11088	0.00	0.44	0.87
11087	0.00	0.42	0.85
11086	0.00	0.00	0.26
11085	0.00	0.00	0.17
11084	0.00	0.00	0.14
11083	0.00	0.00	0.15
11082	0.00	0.00	0.16
11081	0.00	0.00	0.32
11080	0.00	0.00	0.15
11079	0.00	0.00	0.10
11078	0.00	0.00	0.17
11077	0.00	0.00	0.16
11076	0.00	0.00	0.16
11075	0.00	0.00	0.21
11074	0.00	0.01	0.35
11073	0.00	0.00	0.26
11072	0.00	0.00	0.19
11071	0.00	0.00	0.29
11070	0.00	0.00	0.23
11069	0.00	0.00	0.28
11068	0.00	0.02	0.36
11067	0.00	0.10	0.46
11066	0.00	0.00	0.34
11065	0.00	0.13	0.49
11064	0.00	0.12	0.48
11063	0.00	0.20	0.59
11062	0.00	0.00	0.24
11061	0.00	0.38	0.81
11060	0.00	0.11	0.47
11059	0.00	0.00	0.33
11058	0.00	0.00	0.33
11057	0.00	0.15	0.51
11056	0.00	0.00	0.17
11055	0.00	0.07	0.41
11054	0.00	0.08	0.42
11053	0.00	0.02	0.36
11052	0.00	0.02	0.36

Table 19 continued

THE CONCENTRATION OF PARTICULATE COPPER
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051	0.00	0.24	0.63
11050	0.00	0.00	0.25
11049	0.00	0.00	0.23
11048	0.00	0.00	0.11
11047	0.00	0.07	0.54
11046	0.00	0.00	0.20
11045	0.00	0.42	0.93
11044	0.00	0.00	0.27
11043	0.00	0.13	0.60
11042	0.00	0.00	0.29
11041	0.00	0.00	0.34
11040	0.00	0.00	0.33
11039	0.00	0.23	0.62
11038	0.00	0.00	0.28
11037	0.00	0.00	0.28
11036	0.00	0.00	0.28
11035	0.00	0.00	0.15
11034	0.00	0.00	0.13
11033	0.00	0.00	0.30
11032	0.00	0.15	0.64
11031	0.00	0.00	0.28
11030	0.00	0.21	0.60
11029	0.00	0.11	0.47
11028	0.00	0.09	0.45
11027	0.00	0.19	0.68
11026	0.00	0.00	0.31
11025	0.00	0.06	0.42
11024	0.00	0.00	0.31
11023	0.00	0.00	0.21
11022	0.00	0.07	0.43
11021	0.00	0.22	0.63
11020	0.00	0.00	0.41
11019	0.00	0.00	0.41
11018	0.00	0.09	0.58
11017	0.00	0.06	0.53
11016	0.00	0.00	0.24
11015	0.00	0.10	0.46
11014	0.00	0.26	0.54
11013	0.00	0.00	0.33
11012	0.00	0.00	0.33
11011	0.00	0.49	0.94
11010	0.00	0.00	0.32
11009	0.00	0.04	0.38
11008	0.00	0.00	0.17
11007	0.00	0.02	0.24
11006	0.22	0.74	1.19
11005	1.32	2.82	4.23
11004	0.00	0.20	0.69
11003	0.00	0.00	0.16
11002	0.00	0.00	0.33
11001	0.00	0.04	0.40

Table 20

THE CONCENTRATION OF PARTICULATE IRON (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102	1529	1718	1879
11101	1620	1831	2012
11100	462	535	595
11099	493	566	626
11098	920	1039	1140
11097	1113	1255	1376
11096	1578	1790	1971
11095	1499	1687	1848
11094	1692	1903	2084
11093	1681	1892	2074
11092	645	740	821
11091	1285	1450	1591
11090	382	432	472
11089	392	442	483
11088	230	257	277
11087	524	597	657
11086	42	50	54
11085	69	82	90
11084	55	66	72
11083	64	77	85
11082	32	40	44
11081	88	103	113
11080	22	31	35
11079	27	35	39
11078	120	140	154
11077	128	148	162
11076	60	71	77
11075	85	101	111
11074	22	31	35
11073	122	142	156
11072	68	81	89
11071	106	123	136
11070	24	30	32
11069	83	99	109
11068	66	79	87
11067	199	226	246
11066	14	23	27
11065	103	120	132
11064	83	103	117
11063	230	257	277
11062	686	782	862
11061	271	298	318
11060	12	19	21
11059	19	25	27
11058	17	23	25
11057	102	119	131
11056	36	44	48
11055	111	129	141
11054	136	158	175
11053	241	267	288
11052	117	144	164

Table 20 continued

THE CONCENTRATION OF PARTICULATE IRON
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051	111	129	141
11050	177	204	224
11049	188	215	235
11048	105	122	134
11047	310	360	400
11046	10	16	18
11045	403	453	493
11044	104	121	133
11043	269	319	359
11042	15	22	24
11041	138	160	177
11040	12	18	20
11039	454	504	544
11038	22	31	35
11037	142	165	181
11036	7	17	24
11035	84	100	110
11034	9	14	16
11033	92	107	117
11032	13	20	22
11031	57	68	74
11030	76	92	102
11029	382	432	472
11028	56	67	73
11027	199	226	246
11026	64	77	85
11025	133	155	171
11024	39	47	51
11023	210	237	257
11022	95	110	120
11021	441	514	575
11020	68	81	89
11019	269	319	359
11018	362	411	452
11017	331	381	421
11016	15	24	28
11015	173	200	220
11014	53	64	70
11013	101	118	130
11012	92	107	117
11011	454	504	544
11010	45	56	62
11009	118	138	152
11008	72	85	93
11007	114	134	148
11006	747	843	924
11005	2584	2911	3193
11004	382	432	472
11003	237	270	297
11002	70	83	91
11001	220	247	267

Table 21

THE CONCENTRATION OF PARTICULATE MANGANESE (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102	92.5	116.0	139.5
11101	102.5	126.0	149.5
11100	95.5	119.0	142.5
11099	106.5	130.0	153.5
11098	130.6	158.0	185.4
11097	152.6	182.0	211.4
11096	157.6	187.0	216.4
11095	154.6	184.0	213.4
11094	246.6	276.0	305.4
11093	311.8	349.0	386.2
11092	53.9	66.2	78.5
11091	99.3	115.0	130.7
11090	35.7	44.1	52.5
11089	38.3	47.3	56.3
11088	30.9	37.6	44.3
11087	60.3	73.6	86.9
11086	21.0	26.1	31.2
11085	2.3	2.9	3.5
11084	21.1	26.2	31.3
11083	24.3	30.2	36.1
11082	27.1	33.8	40.5
11081	29.4	36.7	44.0
11080	14.6	18.1	21.6
11079	15.8	19.5	23.2
11078	15.9	19.6	23.3
11077	19.0	23.7	28.4
11076	32.4	40.0	47.6
11075	34.3	41.9	49.5
11074	9.7	12.1	14.5
11073	0.8	1.2	1.6
11072	12.4	15.5	18.6
11071	17.6	21.3	25.0
11070	5.2	6.6	8.0
11069	8.0	9.8	11.6
11068	15.4	18.9	22.4
11067	30.7	38.1	45.5
11066	5.0	6.4	7.8
11065	22.9	28.6	34.3
11064	15.3	19.2	23.1
11063	23.1	28.0	32.9
11062	26.7	32.4	38.1
11061	45.3	52.9	60.5
11060	10.0	12.4	14.8
11059	18.9	23.4	27.9
11058	10.0	12.4	14.8
11057	10.0	12.4	14.8
11056	19.1	23.6	28.1
11055	18.2	22.5	26.8
11054	10.8	13.3	15.8
11053	13.7	16.8	19.9
11052	13.8	16.9	20.0

Table 21 continued

THE CONCENTRATION OF PARTICULATE MANGANESE (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051	15.8	19.3	22.8
11050	16.3	20.2	24.1
11049	18.9	23.4	27.9
11048	19.3	23.8	28.3
11047	25.6	31.7	37.8
11046	9.7	12.1	14.5
11045	37.7	46.3	54.9
11044	21.3	26.6	31.9
11043	27.4	34.1	40.8
11042	8.1	10.1	12.1
11041	7.8	9.8	11.8
11040	9.2	11.6	14.0
11039	9.5	11.9	14.3
11038	13.5	16.6	19.7
11037	4.9	6.3	7.7
11036	8.0	10.0	12.0
11035	7.5	9.3	11.1
11034	9.3	11.7	14.1
11033	6.5	8.3	10.1
11032	11.0	13.5	16.0
11031	12.4	15.1	17.8
11030	9.8	12.2	14.6
11029	10.0	12.4	14.8
11028	12.2	15.3	18.4
11027	23.4	29.1	34.8
11026	9.4	11.8	14.2
11025	6.1	7.7	9.3
11024	7.0	9.0	11.0
11023	7.5	9.5	11.5
11022	9.0	11.4	13.8
11021	15.0	18.7	22.4
11020	10.7	13.6	16.5
11019	14.4	18.1	21.8
11018	26.3	33.0	39.7
11017	24.1	29.8	35.5
11016	7.3	9.3	11.3
11015	8.5	10.7	12.9
11014	6.8	8.8	10.8
11013	11.1	13.8	16.5
11012	8.5	10.9	13.3
11011	22.2	26.9	31.6
11010	5.7	7.3	8.9
11009	7.8	9.8	11.8
11008	4.5	6.1	7.7
11007	6.6	8.6	10.6
11006	18.8	22.5	26.2
11005	98.6	108.0	117.4
11004	16.4	20.1	23.8
11003	15.5	19.2	22.9
11002	13.5	16.8	20.1
11001	13.0	15.9	18.8

Table 22

THE CONCENTRATION OF PARTICULATE MOLYBDENUM (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102		< 0.05	
11101		< 0.06	
11100	0.00	0.02	0.06
11099	0.00	0.02	0.06
11098		< 0.03	
11097		< 0.04	
11096		< 0.06	
11095		< 0.07	
11094	0.00	0.08	0.24
11093		< 0.08	
11092	0.00	0.01	0.03
11091	0.13	0.25	0.37
11090		< 0.06	
11089	0.01	0.05	0.09
11088	0.00	0.02	0.06
11087		< 0.09	
11086		< 0.03	
11085		< 0.03	
11084		< 0.02	
11083		< 0.02	
11082		< 0.08	
11081	0.00	0.02	0.06
11080		< 0.02	
11079		< 0.02	
11078		< 0.03	
11077		< 0.03	
11076		< 0.03	
11075		< 0.02	
11074		< 0.03	
11073		< 0.04	
11072		< 0.04	
11071		< 0.03	
11070		< 0.03	
11069		< 0.02	
11068		< 0.06	
11067		< 0.05	
11066		< 0.05	
11065		< 0.04	
11064		< 0.04	
11063		< 0.05	
11062	0.00	0.02	0.06
11061		< 0.04	
11060		< 0.02	
11059		< 0.03	
11058		< 0.03	
11057		< 0.04	
11056		< 0.03	
11055		< 0.05	
11054		< 0.02	
11053		< 0.03	
11052		< 0.04	

Table 22 continued

THE CONCENTRATION OF PARTICULATE MOLYBDENUM
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051		< 0.06	
11050		< 0.20	
11049		< 0.20	
11048		< 0.09	
11047		< 0.10	
11046		< 0.05	
11045		< 0.80	
11044		< 0.60	
11043		< 0.05	
11042		< 0.03	
11041		< 0.10	
11040		< 0.03	
11039		< 0.06	
11038		< 0.02	
11037		< 0.05	
11036		< 0.03	
11035		< 0.09	
11034		< 0.03	
11033		< 0.05	
11032		< 0.03	
11031		< 0.04	
11030		< 0.03	
11029		< 0.40	
11028		< 0.03	
11027		< 0.60	
11026		< 0.06	
11025		< 0.05	
11024	0.00	0.21	0.41
11023		< 0.05	
11022		< 0.06	
11021		< 0.06	
11020		< 0.04	
11019		< 0.02	
11018		< 0.08	
11017	0.01	0.03	0.05
11016		< 0.06	
11015		< 0.70	
11014		< 0.06	
11013		< 0.06	
11012		< 0.06	
11011		< 0.70	
11010		< 0.04	
11009		< 0.07	
11008		< 0.05	
11007		< 0.06	
11006		< 0.80	
11005	0.00	0.21	0.61
11004		< 0.07	
11003		< 0.07	
11002		< 0.06	
11001		< 0.06	

Table 23

THE CONCENTRATION OF PARTICULATE NICKEL
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102	1.74	2.50	3.09
11101	2.04	2.80	3.39
11100	0.69	1.00	1.20
11099	0.89	1.20	1.40
11098	1.36	1.90	2.29
11097	1.96	2.50	2.89
11096	1.76	2.30	2.69
11095	1.64	2.40	2.99
11094	3.14	3.90	4.49
11093	4.01	5.00	5.78
11092	0.65	0.92	1.08
11091	1.16	1.70	2.09
11090	0.46	0.73	0.89
11089	0.50	0.77	0.93
11088	0.26	0.46	0.56
11087	0.63	0.94	1.14
11086	0.07	0.20	0.24
11085	0.00	0.11	0.13
11084	0.08	0.24	0.30
11083	0.10	0.26	0.32
11082	0.08	0.24	0.30
11081	0.07	0.20	0.24
11080	0.09	0.22	0.26
11079	0.04	0.17	0.21
11078	0.13	0.29	0.35
11077	0.14	0.30	0.36
11076	0.03	0.16	0.20
11075	0.04	0.17	0.21
11074	0.09	0.25	0.31
11073	0.00	0.10	0.12
11072	0.17	0.35	0.43
11071	0.25	0.43	0.51
11070	0.09	0.22	0.26
11069	0.01	0.14	0.18
11068	0.10	0.26	0.32
11067	0.18	0.36	0.44
11066	0.12	0.28	0.34
11065	0.05	0.18	0.22
11064	0.07	0.20	0.24
11063	0.28	0.48	0.58
11062	0.42	0.64	0.76
11061	0.79	1.10	1.30
11060	0.03	0.16	0.20
11059	0.04	0.17	0.21
11058	0.05	0.18	0.22
11057	0.11	0.27	0.33
11056	0.08	0.24	0.30
11055	0.13	0.29	0.35
11054	0.11	0.27	0.33
11053	0.26	0.46	0.56
11052	0.11	0.27	0.33

Table 23 continued

THE CONCENTRATION OF PARTICULATE NICKEL
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051	0.14	0.30	0.36
11050	0.21	0.39	0.47
11049	0.19	0.37	0.45
11048	0.16	0.32	0.38
11047	0.43	0.70	0.86
11046	0.10	0.26	0.32
11045	0.69	1.00	1.20
11044	0.27	0.47	0.57
11043	0.47	0.74	0.90
11042	0.05	0.18	0.22
11041	0.15	0.33	0.41
11040	0.12	0.30	0.38
11039	0.53	0.84	1.04
11038	0.09	0.22	0.26
11037	0.11	0.24	0.28
11036	0.07	0.20	0.24
11035	0.02	0.15	0.19
11034	0.00	0.11	0.15
11033	0.00	0.08	0.10
11032	0.01	0.17	0.23
11031	0.00	0.09	0.11
11030	0.01	0.14	0.18
11029	0.22	0.42	0.52
11028	0.00	0.07	0.09
11027	0.19	0.37	0.45
11026	0.03	0.16	0.20
11025	0.01	0.14	0.18
11024	0.00	0.03	0.05
11023	0.03	0.21	0.29
11022	0.01	0.17	0.23
11021	0.39	0.70	0.90
11020	0.04	0.22	0.30
11019	0.38	0.63	0.77
11018	0.01	0.19	0.27
11017	0.26	0.46	0.56
11016	0.00	0.14	0.20
11015	0.01	0.19	0.27
11014	0.00	0.14	0.20
11013	0.21	0.41	0.51
11012	0.04	0.17	0.21
11011	0.96	1.50	1.89
11010	0.00	0.11	0.15
11009	0.03	0.21	0.29
11008	0.00	0.07	0.09
11007	0.02	0.15	0.19
11006	0.64	0.95	1.15
11005	0.32	0.63	0.83
11004	0.34	0.65	0.85
11003	0.24	0.51	0.67
11002	0.03	0.16	0.20
11001	0.19	0.39	0.49

Table 24

THE CONCENTRATION OF PARTICULATE LEAD (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102	1.61	2.10	2.49
11101	2.09	2.80	3.39
11100	1.01	1.50	1.89
11099	0.91	1.40	1.79
11098	1.71	2.20	2.59
11097	2.49	3.20	3.79
11096	3.76	4.70	5.48
11095	5.92	7.30	8.48
11094	2.89	3.60	4.19
11093	5.34	6.50	7.48
11092	1.49	2.20	2.79
11091	2.94	4.10	5.08
11090	0.42	0.64	0.80
11089	0.41	0.63	0.79
11088	0.28	0.43	0.53
11087	0.67	0.93	1.13
11086	0.00	0.06	0.08
11085	0.00	0.05	0.07
11084	0.03	0.09	0.11
11083	0.12	0.23	0.29
11082	0.11	0.22	0.28
11081	0.08	0.16	0.20
11080	0.00	0.05	0.07
11079	0.00	0.04	0.06
11078	0.04	0.12	0.16
11077	0.06	0.14	0.18
11076	0.06	0.17	0.23
11075	0.03	0.11	0.15
11074	0.00	0.03	0.05
11073	0.01	0.07	0.09
11072	0.01	0.07	0.09
11071	0.09	0.20	0.26
11070	0.00	0.02	0.04
11069	0.01	0.07	0.09
11068	0.00	0.06	0.08
11067	0.22	0.35	0.43
11066		< 0.01	
11065	0.12	0.23	0.29
11064	0.06	0.17	0.23
11063	0.24	0.39	0.49
11062	0.46	0.68	0.84
11061	0.62	1.00	1.29
11060	0.02	0.08	0.10
11059	0.04	0.10	0.12
11058	0.01	0.07	0.09
11057	0.21	0.34	0.42
11056	0.06	0.14	0.18
11055	0.07	0.18	0.24
11054	0.33	0.48	0.58
11053	0.36	0.51	0.61
11052	0.47	0.67	0.81

Table 24 continued

THE CONCENTRATION OF PARTICULATE LEAD (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051	0.35	0.50	0.60
11050	0.28	0.43	0.53
11049	0.23	0.36	0.44
11048	0.16	0.29	0.37
11047	0.42	0.64	0.80
11046	0.05	0.16	0.22
11045	0.48	0.70	0.86
11044	0.33	0.50	0.62
11043	0.48	0.70	0.86
11042	0.03	0.09	0.11
11041	0.17	0.28	0.34
11040	0.13	0.24	0.30
11039	0.53	0.75	0.91
11038	0.00	0.01	0.03
11037	0.22	0.37	0.47
11036		< 0.01	
11035	0.00	0.06	0.08
11034		< 0.01	
11033	0.00	0.04	0.06
11032		< 0.01	
11031		< 0.01	
11030	0.06	0.14	0.18
11029	0.48	0.70	0.86
11028	0.02	0.10	0.14
11027	0.17	0.30	0.38
11026	0.17	0.28	0.34
11025	0.10	0.21	0.27
11024	0.01	0.09	0.13
11023	0.06	0.14	0.18
11022	0.08	0.16	0.20
11021	0.10	0.18	0.22
11020	0.08	0.16	0.20
11019	0.15	0.26	0.32
11018	0.66	0.90	1.08
11017	0.20	0.33	0.41
11016	0.02	0.10	0.14
11015	0.00	0.03	0.05
11014	0.04	0.12	0.16
11013	0.01	0.07	0.09
11012	0.13	0.21	0.25
11011	0.19	0.32	0.40
11010	0.11	0.19	0.23
11009	0.09	0.17	0.21
11008	0.08	0.16	0.20
11007	0.10	0.21	0.27
11006	0.24	0.37	0.45
11005	6.59	7.30	7.89
11004	0.14	0.25	0.31
11003	0.12	0.23	0.29
11002		< 0.01	
11001	0.32	0.47	0.57

Table 25

THE CONCENTRATION OF PARTICULATE SCANDIUM (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102	0.5665	0.6068	0.6471
11101	0.5772	0.6376	0.6981
11100	0.1381	0.1543	0.1704
11099	0.1464	0.1625	0.1786
11098	0.2682	0.3085	0.3489
11097	0.3402	0.3805	0.4208
11096	0.4949	0.5554	0.6158
11095	0.4538	0.5142	0.5747
11094	0.5052	0.5657	0.6261
11093	0.4949	0.5554	0.6158
11092	0.1958	0.2160	0.2361
11091	0.4225	0.4628	0.5031
11090	0.1340	0.1481	0.1622
11089	0.1360	0.1502	0.1643
11088	0.0783	0.0864	0.0945
11087	0.1773	0.1975	0.2176
11086	0.0157	0.0175	0.0193
11085	0.0149	0.0166	0.0182
11084	0.0216	0.0237	0.0257
11083	0.0247	0.0267	0.0288
11082	0.0120	0.0134	0.0148
11081	0.0268	0.0288	0.0308
11080	0.0092	0.0102	0.0112
11079	0.0095	0.0105	0.0115
11078	0.0495	0.0555	0.0616
11077	0.0515	0.0576	0.0636
11076	0.0186	0.0206	0.0226
11075	0.0227	0.0247	0.0267
11074	0.0096	0.0106	0.0116
11073	0.0128	0.0142	0.0156
11072	0.0279	0.0319	0.0359
11071	0.0433	0.0473	0.0513
11070	0.0094	0.0104	0.0114
11069	0.0216	0.0237	0.0257
11068	0.0247	0.0267	0.0288
11067	0.0649	0.0710	0.0770
11066	0.0069	0.0077	0.0085
11065	0.0237	0.0257	0.0277
11064	0.0392	0.0432	0.0472
11063	0.1010	0.1111	0.1212
11062	0.2991	0.3394	0.3797
11061	0.1165	0.1286	0.1407
11060	0.0048	0.0055	0.0061
11059	0.0060	0.0066	0.0072
11058	0.0061	0.0067	0.0073
11057	0.0268	0.0288	0.0308
11056	0.0132	0.0146	0.0160
11055	0.0361	0.0401	0.0441
11054	0.0639	0.0720	0.0801
11053	0.1093	0.1214	0.1335
11052	0.0485	0.0545	0.0606

Table 25 continued

THE CONCENTRATION OF PARTICULATE SCANDIUM
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051	0.0453	0.0494	0.0534
11050	0.0742	0.0823	0.0903
11049	0.0742	0.0823	0.0903
11048	0.0402	0.0442	0.0483
11047	0.1258	0.1399	0.1540
11046	0.0053	0.0059	0.0065
11045	0.1515	0.1676	0.1838
11044	0.0422	0.0463	0.0503
11043	0.1165	0.1286	0.1407
11042	0.0045	0.0051	0.0057
11041	0.0412	0.0453	0.0493
11040	0.0042	0.0046	0.0050
11039	0.1423	0.1584	0.1745
11038	0.0075	0.0083	0.0091
11037	0.0381	0.0422	0.0462
11036	0.0032	0.0036	0.0040
11035	0.0247	0.0267	0.0288
11034	0.0028	0.0030	0.0032
11033	0.0268	0.0288	0.0308
11032	0.0046	0.0050	0.0054
11031	0.0134	0.0148	0.0162
11030	0.0216	0.0237	0.0257
11029	0.1185	0.1306	0.1427
11028	0.0175	0.0195	0.0216
11027	0.0650	0.0730	0.0811
11026	0.0216	0.0237	0.0257
11025	0.0443	0.0483	0.0524
11024	0.0125	0.0139	0.0153
11023	0.0639	0.0699	0.0760
11022	0.0309	0.0350	0.0390
11021	0.1412	0.1553	0.1694
11020	0.0206	0.0226	0.0246
11019	0.0887	0.0987	0.1088
11018	0.1165	0.1286	0.1407
11017	0.1062	0.1183	0.1304
11016	0.0059	0.0065	0.0071
11015	0.0567	0.0627	0.0688
11014	0.0165	0.0185	0.0205
11013	0.0309	0.0350	0.0390
11012	0.0289	0.0329	0.0369
11011	0.1464	0.1625	0.1786
11010	0.0140	0.0156	0.0172
11009	0.0392	0.0432	0.0472
11008	0.0237	0.0257	0.0277
11007	0.0361	0.0401	0.0441
11006	0.2587	0.2869	0.3152
11005	0.8248	0.9256	1.0264
11004	0.1278	0.1419	0.1560
11003	0.0773	0.0854	0.0934
11002	0.0196	0.0216	0.0236
11001	0.0649	0.0710	0.0770

Table 26

THE CONCENTRATION OF PARTICULATE TIN
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102		< 3.00	
11101		< 3.00	
11100		< 0.80	
11099		< 0.50	
11098		< 1.00	
11097		< 2.00	
11096		< 2.00	
11095		< 3.00	
11094		< 2.00	
11093		< 2.00	
11092		< 2.00	
11091		< 1.00	
11090		< 0.60	
11089		< 0.60	
11088		< 0.60	
11087		< 2.00	
11086		< 0.50	
11085		< 0.70	
11084		< 0.60	
11083		< 0.60	
11082		< 0.60	
11081		< 0.50	
11080		< 0.40	
11079		< 0.30	
11078		< 0.30	
11077		< 0.50	
11076		< 0.50	
11075		< 0.40	
11074		< 0.30	
11073		< 0.40	
11072		< 0.80	
11071		< 0.40	
11070		< 0.50	
11069		< 0.40	
11068		< 0.50	
11067		< 0.80	
11066		< 0.70	
11065		< 1.00	
11064		< 1.00	
11063		< 1.00	
11062		< 2.00	
11061		< 1.00	
11060		< 1.00	
11059		< 0.30	
11058		< 0.50	
11057		< 0.50	
11056		< 1.00	
11055		< 2.00	
11054		< 0.70	
11053		< 1.00	
11052		< 4.00	
11051		< 2.00	

Table 26 continued

THE CONCENTRATION OF PARTICULATE TIN
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11050		< 0.80	
11049		< 0.50	
11048		< 0.80	
11047		< 0.50	
11046		< 0.30	
11045		< 2.00	
11044		< 0.60	
11043		< 0.50	
11042		< 0.40	
11041		< 0.80	
11040		< 0.05	
11039		< 0.70	
11038		< 0.50	
11037		< 0.50	
11036		< 0.70	
11035		< 0.80	
11034		< 0.30	
11033		< 0.80	
11032		< 0.40	
11031		< 1.00	
11030		< 0.50	
11029		< 0.70	
11028		< 0.70	
11027		< 1.00	
11026		< 0.70	
11025		< 1.00	
11024		< 0.70	
11023		< 2.00	
11022		< 2.00	
11021		< 2.00	
11020		< 0.70	
11019		< 0.70	
11018		< 1.00	
11017		< 0.70	
11016		< 1.00	
11015		< 2.00	
11014		< 2.00	
11013		< 0.70	
11012		< 0.80	
11011		< 2.00	
11010		< 0.60	
11009		< 1.00	
11008		< 0.50	
11007		< 0.50	
11006		< 2.00	
11005		< 2.00	
11004		< 0.70	
11003		< 0.30	
11002		< 1.00	
11001		< 0.60	

Table 27

THE CONCENTRATION OF PARTICULATE THORIUM (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102	0.4538	0.5142	0.5747
11101	0.4846	0.5451	0.6056
11100	0.1330	0.1471	0.1612
11099	0.1392	0.1553	0.1714
11098	0.2781	0.2983	0.3184
11097	0.3299	0.3702	0.4106
11096	0.4538	0.5142	0.5747
11095	0.4431	0.4834	0.5237
11094	0.4949	0.5554	0.6158
11093	0.4949	0.5554	0.6158
11092	0.1855	0.2057	0.2258
11091	0.3094	0.3497	0.3900
11090	0.0969	0.1070	0.1170
11089	0.1010	0.1111	0.1212
11088	0.0587	0.0648	0.0708
11087	0.1371	0.1512	0.1653
11086	0.0103	0.0123	0.0144
11085	0.0103	0.0123	0.0144
11084	0.0155	0.0175	0.0195
11083	0.0165	0.0183	0.0201
11082	0.0094	0.0106	0.0118
11081	0.0196	0.0216	0.0236
11080	0.0066	0.0074	0.0082
11079	0.0067	0.0075	0.0083
11078	0.0422	0.0463	0.0503
11077	0.0443	0.0483	0.0524
11076	0.0147	0.0164	0.0180
11075	0.0173	0.0191	0.0209
11074	0.0075	0.0083	0.0091
11073	0.0098	0.0108	0.0118
11072	0.0247	0.0267	0.0288
11071	0.0371	0.0411	0.0452
11070	0.0069	0.0079	0.0089
11069	0.0155	0.0175	0.0195
11068	0.0176	0.0216	0.0256
11067	0.0495	0.0555	0.0616
11066	0.0021	0.0041	0.0061
11065	0.0114	0.0154	0.0195
11064	0.0289	0.0329	0.0369
11063	0.0835	0.0936	0.1037
11062	0.2472	0.2674	0.2876
11061	0.0948	0.1049	0.1150
11060	0.0038	0.0044	0.0050
11059	0.0051	0.0063	0.0075
11058	0.0031	0.0043	0.0055
11057	0.0216	0.0237	0.0257
11056	0.0083	0.0097	0.0111
11055	0.0258	0.0298	0.0339
11054	0.0505	0.0566	0.0626
11053	0.0907	0.1008	0.1109
11052	0.0371	0.0411	0.0452

Table 27 continued

THE CONCENTRATION OF PARTICULATE THORIUM
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051	0.0371	0.0411	0.0452
11050	0.0639	0.0699	0.0760
11049	0.0639	0.0720	0.0801
11048	0.0340	0.0381	0.0421
11047	0.1093	0.1214	0.1335
11046	0.0039	0.0045	0.0051
11045	0.1350	0.1491	0.1632
11044	0.0371	0.0411	0.0452
11043	0.1041	0.1162	0.1283
11042	0.0030	0.0040	0.0050
11041	0.0350	0.0391	0.0431
11040	0.0030	0.0034	0.0038
11039	0.1206	0.1347	0.1488
11038	0.0047	0.0063	0.0079
11037	0.0299	0.0339	0.0380
11036		< 0.0050	
11035	0.0186	0.0226	0.0267
11034	0.0017	0.0023	0.0029
11033	0.0227	0.0247	0.0267
11032	0.0034	0.0044	0.0054
11031	0.0083	0.0103	0.0123
11030	0.0165	0.0185	0.0205
11029	0.0969	0.1070	0.1170
11028	0.0124	0.0144	0.0164
11027	0.0526	0.0586	0.0647
11026	0.0186	0.0206	0.0226
11025	0.0350	0.0391	0.0431
11024	0.0081	0.0101	0.0121
11023	0.0515	0.0576	0.0636
11022	0.0207	0.0247	0.0287
11021	0.1195	0.1316	0.1437
11020	0.0135	0.0175	0.0215
11019	0.0691	0.0771	0.0852
11018	0.0876	0.0977	0.1078
11017	0.0856	0.0956	0.1057
11016		< 0.0050	
11015	0.0485	0.0545	0.0606
11014	0.0145	0.0185	0.0225
11013	0.0248	0.0288	0.0328
11012	0.0237	0.0278	0.0318
11011	0.1185	0.1306	0.1427
11010	0.0124	0.0144	0.0164
11009	0.0320	0.0360	0.0400
11008	0.0186	0.0206	0.0226
11007	0.0268	0.0309	0.0349
11006	0.1711	0.1892	0.2074
11005	0.6183	0.6788	0.7393
11004	0.0907	0.1008	0.1109
11003	0.0608	0.0668	0.0729
11002	0.0145	0.0185	0.0225
11001	0.0515	0.0576	0.0636

Table 28

THE CONCENTRATION OF PARTICULATE URANIUM
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102	0.1144	0.1265	0.1386
11101	0.1227	0.1368	0.1509
11100	0.0402	0.0442	0.0483
11099	0.0402	0.0442	0.0483
11098	0.0752	0.0833	0.0914
11097	0.0856	0.0956	0.1057
11096	0.1258	0.1399	0.1540
11095	0.1556	0.1718	0.1879
11094	0.1391	0.1532	0.1674
11093	0.1742	0.1923	0.2105
11092	0.0577	0.0638	0.0698
11091	0.1093	0.1214	0.1335
11090	0.0269	0.0329	0.0390
11089	0.0289	0.0329	0.0369
11088	0.0114	0.0154	0.0195
11087	0.0402	0.0463	0.0523
11086	0.0036	0.0052	0.0069
11085	0.0066	0.0084	0.0102
11084	0.0044	0.0057	0.0069
11083	0.0052	0.0060	0.0068
11082		< 0.0100	
11081	0.0073	0.0085	0.0097
11080	0.0021	0.0035	0.0049
11079	0.0029	0.0039	0.0049
11078	0.0122	0.0136	0.0150
11077	0.0114	0.0134	0.0154
11076	0.0057	0.0073	0.0089
11075	0.0000	0.0113	0.0315
11074	0.0024	0.0040	0.0056
11073	0.0105	0.0119	0.0133
11072	0.0068	0.0086	0.0105
11071	0.0114	0.0134	0.0154
11070	0.0027	0.0041	0.0055
11069	0.0000	0.0083	0.0204
11068	0.0032	0.0072	0.0112
11067	0.0176	0.0216	0.0256
11066	0.0011	0.0031	0.0051
11065	0.0081	0.0095	0.0109
11064	0.0066	0.0080	0.0094
11063	0.0196	0.0237	0.0277
11062	0.0691	0.0771	0.0852
11061	0.0248	0.0288	0.0328
11060	0.0014	0.0024	0.0034
11059	0.0018	0.0036	0.0054
11058	0.0020	0.0034	0.0048
11057	0.0067	0.0087	0.0108
11056	0.0034	0.0046	0.0058
11055	0.0104	0.0144	0.0184
11054	0.0155	0.0175	0.0195
11053	0.0237	0.0278	0.0318
11052	0.0124	0.0144	0.0164

Table 28 continued

THE CONCENTRATION OF PARTICULATE URANIUM (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051	0.0114	0.0134	0.0154
11050		< 0.0500	
11049		< 0.0300	
11048	0.0095	0.0216	0.0337
11047	0.0310	0.0370	0.0431
11046		< 0.0050	
11045		< 0.1000	
11044		< 0.0900	
11043	0.0289	0.0329	0.0369
11042	0.0011	0.0031	0.0051
11041		< 0.0300	
11040	0.0011	0.0031	0.0051
11039	0.0004	0.0206	0.0407
11038		< 0.0020	
11037	0.0073	0.0134	0.0194
11036	0.0018	0.0036	0.0054
11035		< 0.0200	
11034	0.0062	0.0082	0.0102
11033	0.0062	0.0082	0.0102
11032	0.0052	0.0072	0.0092
11031	0.0052	0.0072	0.0092
11030	0.0042	0.0062	0.0082
11029		< 0.0500	
11028	0.0062	0.0082	0.0102
11027	0.0145	0.0185	0.0225
11026		< 0.0100	
11025	0.0073	0.0113	0.0153
11024	0.0033	0.0045	0.0057
11023	0.0114	0.0134	0.0154
11022	0.0093	0.0113	0.0133
11021		< 0.0500	
11020	0.0052	0.0093	0.0133
11019	0.0155	0.0195	0.0236
11018	0.0217	0.0278	0.0338
11017	0.0196	0.0237	0.0277
11016		< 0.0050	
11015		< 0.0900	
11014	0.0031	0.0051	0.0072
11013	0.0052	0.0072	0.0092
11012	0.0062	0.0082	0.0102
11011		< 0.0800	
11010	0.0031	0.0051	0.0072
11009	0.0052	0.0072	0.0092
11008	0.0021	0.0041	0.0061
11007	0.0062	0.0082	0.0102
11006		< 0.1000	
11005	0.1341	0.1543	0.1744
11004	0.0196	0.0237	0.0277
11003	0.0165	0.0206	0.0246
11002	0.0052	0.0072	0.0092
11001	0.0269	0.0329	0.0390

Table 29

THE CONCENTRATION OF PARTICULATE ZINC
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102	5.59	8.22	9.65
11101	5.79	8.42	9.86
11100	1.29	2.88	3.49
11099	1.80	3.39	4.00
11098	4.94	7.29	8.52
11097	6.25	8.83	10.26
11096	7.80	10.89	12.73
11095	7.29	10.38	12.21
11094	12.25	15.52	17.55
11093	10.93	13.98	15.81
11092	4.77	7.39	8.83
11091	9.22	12.54	14.58
11090	0.88	2.77	3.59
11089	1.60	3.49	4.31
11088	0.70	2.36	2.98
11087	1.88	4.00	5.03
11086	0.00	0.15	0.68
11085	0.00	0.33	0.85
11084	0.00	0.55	1.17
11083	0.00	0.45	1.04
11082	0.00	0.42	1.19
11081	0.00	0.73	1.29
11080	0.00	0.73	1.27
11079	0.00	0.50	1.05
11078	0.00	0.87	1.64
11077	0.00	0.74	1.30
11076	0.00	0.60	1.12
11075	0.00	0.53	1.08
11074	0.00	0.53	1.08
11073	0.00	0.07	0.55
11072	0.00	0.59	1.13
11071	0.00	0.81	1.44
11070	0.00	0.21	0.75
11069	0.00	0.22	0.92
11068	0.00	0.56	1.12
11067	0.00	1.06	1.62
11066	0.00	0.22	0.94
11065		< 1.00	
11064	0.00	0.71	1.94
11063		< 2.00	
11062	0.50	2.66	3.69
11061	0.00	0.92	1.74
11060	0.00	0.36	0.90
11059	0.00	0.12	0.65
11058	0.00	0.27	0.81
11057	0.00	0.34	0.90
11056	0.00	0.37	0.95
11055	0.00	0.40	0.98
11054	0.00	0.50	1.33
11053	0.00	0.95	1.55
11052		< 1.00	

Table 29 continued

THE CONCENTRATION OF PARTICULATE ZINC
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS AT LEAST
THE 95% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051	0.00	0.43	1.01
11050	0.00	0.73	1.37
11049	0.00	0.67	1.31
11048	0.00	0.15	0.78
11047	0.00	1.12	2.15
11046	0.00	0.11	0.84
11045	0.00	2.15	3.38
11044	0.00	0.79	1.46
11043	0.00	1.12	2.15
11042	0.00	0.04	0.56
11041	0.00	0.25	0.83
11040	0.00	0.20	0.68
11039	0.00	1.74	2.56
11038	0.00	0.30	0.92
11037	0.00	0.50	1.11
11036		< 0.60	
11035	0.00	0.00	0.53
11034	0.00	1.02	1.64
11033	0.00	0.30	0.92
11032	0.00	0.23	1.01
11031		< 0.50	
11030	0.00	0.33	0.89
11029	0.00	1.43	2.25
11028	0.00	0.30	0.92
11027	0.00	0.81	1.84
11026	0.00	0.42	1.00
11025	0.00	0.40	1.23
11024	0.00	0.50	1.33
11023		< 0.80	
11022		< 2.00	
11021	0.00	1.64	2.66
11020	0.00	0.40	1.23
11019	0.00	1.33	2.36
11018	0.00	1.12	2.15
11017	0.00	1.02	1.85
11016		< 0.40	
11015	0.00	1.22	2.05
11014		< 0.90	
11013	0.00	0.50	1.13
11012	0.00	0.30	0.92
11011	0.00	1.64	2.46
11010		< 0.50	
11009		< 0.90	
11008	0.00	0.37	0.70
11007	0.57	2.16	2.77
11006	2.24	4.82	6.25
11005	11.35	14.90	17.14
11004	0.68	3.08	4.31
11003	0.00	1.43	2.26
11002		< 0.90	
11001	0.00	0.92	1.54

Table 30

BLANK CONCENTRATIONS FOR DISSOLVED CADMIUM (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE
ONE SIGMA LEVEL

SAMPLE NUMBER		MINIMUM	BEST VALUE	MAXIMUM
B-3	1		< 0.007	
B-9	1		< 0.007	
B-9	1		< 0.007	
B-11	2		< 0.007	
B-5	2		< 0.007	
B-7	2		< 0.007	
B-11	3		< 0.007	
B-3	3		< 0.007	
B-7	3		< 0.007	
B-17	4		< 0.007	
B-19	4		< 0.007	
B-21	4	0.019	0.021	0.023
B-21	5		< 0.007	
B-25	5		< 0.007	
B-11	6		< 0.007	
B-13	6		< 0.007	
B-21	6		< 0.007	
B-4	7	0.039	0.043	0.047
B-6	7	0.019	0.021	0.023
B-8	7	0.019	0.021	0.023
B-10	8		< 0.007	
B-12	8		< 0.007	
B-14	8		< 0.007	

Table 31

BLANK CONCENTRATIONS FOR DISSOLVED COBALT (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE
ONE SIGMA LEVEL

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
B-3B 1	0.0104	0.0110	0.0116
B-7B 1	0.0050	0.0053	0.0056
B-9B 1	0.0068	0.0072	0.0076
B-11A 2	0.0055	0.0058	0.0061
B-5A 2	0.0050	0.0053	0.0056
B-7A 2	0.0082	0.0087	0.0092
B-11B 3	0.0060	0.0063	0.0066
B-3B 3	0.0117	0.0123	0.0129
B-7B 3	0.0055	0.0058	0.0061
B-17A 4	0.0280	0.0300	0.0320
B-19A 4	0.0069	0.0073	0.0077
B-21A 4	0.0077	0.0081	0.0085
B-21B 5	0.0074	0.0078	0.0082
B-25B 5	0.0071	0.0075	0.0079
B-7B 5	0.0063	0.0066	0.0069
B-11B 6	0.0090	0.0095	0.0100
B-13B 6	0.0095	0.0100	0.0105
B-17B 6	0.0380	0.0400	0.0420
B-4A 7	0.0104	0.0110	0.0116
B-6A 7	0.0090	0.0095	0.0100
B-8A 7	0.0220	0.0240	0.0260
B-10A 8	0.0152	0.0160	0.0168
B-12A 8	0.0270	0.0280	0.0290
B-14A 8	0.0140	0.0147	0.0154

Table 32

BLANK CONCENTRATIONS FOR DISSOLVED CHROMIUM
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE
ONE SIGMA LEVEL

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
B-3B 1	1.47	1.55	1.63
B-7B 1	1.30	1.37	1.44
B-9B 1	1.48	1.56	1.64
B-11A 2	1.33	1.40	1.47
B-5A 2	1.46	1.54	1.62
B-7A 2	1.26	1.33	1.40
B-11B 3	1.42	1.49	1.56
B-3B 3	1.46	1.54	1.62
B-7B 3	1.50	1.58	1.66
B-17A 4	1.48	1.56	1.64
B-19A 4	1.49	1.57	1.65
B-21A 4	1.46	1.54	1.62
B-21B 5	1.36	1.43	1.50
B-25B 5	1.62	1.71	1.80
B-7B 5	1.62	1.71	1.80
B-11B 6	1.46	1.54	1.62
B-13B 6	1.47	1.55	1.63
B-17B 6	1.47	1.55	1.63
B-4A 7	1.40	1.47	1.54
B-6A 7	1.46	1.54	1.62
B-8A 7	1.62	1.71	1.80
B-10A 8	1.59	1.67	1.75
B-12A 8	1.48	1.56	1.64
B-14A 8	1.59	1.67	1.75

Table 33

BLANK CONCENTRATIONS FOR DISSOLVED COPPER
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE
ONE SIGMA LEVEL

SAMPLE NUMBER		MINIMUM	BEST VALUE	MAXIMUM
B-3	1		< 0.08	
B-9	1		< 0.08	
B-9	1		< 0.08	
B-11	2		< 0.08	
B-5	2		< 0.08	
B-7	2		< 0.08	
B-11	3	0.07	0.08	0.09
B-3	3		< 0.08	
B-7	3	.	.	.
B-17	4	0.10	0.12	0.14
B-19	4	0.14	0.16	0.18
B-21	4	0.12	0.14	0.16
B-21	5		< 0.08	
B-25	5		< 0.08	
B-11	6	0.39	0.43	0.47
B-13	6	0.17	0.19	0.21
B-21	6	0.35	0.39	0.43
B-4	7		< 0.08	
B-6	7		< 0.08	
B-8	7		< 0.08	
B-10	8		< 0.08	
B-12	8		< 0.08	
B-14	8		< 0.08	

Table 34

BLANK CONCENTRATIONS FOR DISSOLVED IRON
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE
ONE SIGMA LEVEL

SAMPLE NUMBER		MINIMUM	BEST VALUE	MAXIMUM
B-3B	1	0.94	1.00	1.06
B-7B	1	0.96	1.02	1.08
B-9B	1	3.50	3.70	3.90
B-11A	2	1.15	1.25	1.35
B-5A	2	1.20	1.30	1.40
B-7A	2	0.67	0.75	0.83
B-11B	3	0.52	0.59	0.66
B-3B	3	1.14	1.20	1.26
B-7B	3	0.75	0.80	0.85
B-17A	4	0.84	0.95	1.06
B-19A	4	1.50	1.70	1.90
B-21A	4	1.00	1.10	1.20
B-21B	5	0.53	0.68	0.83
B-25B	5	1.40	1.50	1.60
B-7B	5	1.00	1.10	1.20
B-11B	6	1.44	1.53	1.62
B-13B	6	0.83	0.90	0.97
B-17B	6	1.03	1.10	1.17
B-4A	7	0.80	0.89	0.98
B-6A	7	1.13	1.24	1.35
B-8A	7	1.78	1.88	1.98
B-10A	8	1.93	2.03	2.13
B-12A	8	0.70	0.79	0.88
B-14A	8	1.40	1.50	1.60

Table 35

BLANK CONCENTRATIONS FOR DISSOLVED MANGANESE (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE
ONE SIGMA LEVEL

SAMPLE NUMBER		MINIMUM	BEST VALUE	MAXIMUM
B-3	1	0.700	0.770	0.840
B-9	1	0.440	0.480	0.520
B-9	1	0.400	0.440	0.480
B-11	2	0.590	0.700	0.810
B-5	2	0.600	0.700	0.800
B-7	2	0.700	0.800	0.900
B-11	3		< 0.008	
B-3	3		< 0.008	
B-7	3		< 0.008	
B-17	4	0.390	0.430	0.470
B-19	4	0.330	0.370	0.410
B-21	4	0.240	0.270	0.300
B-21	5	0.180	0.200	0.220
B-25	5	0.140	0.160	0.180
B-11	6		< 0.008	
B-13	6		< 0.008	
B-21	6		< 0.008	
B-4	7	0.620	0.690	0.760
B-6	7		< 0.008	
B-8	7		< 0.008	
B-10	8		< 0.008	
B-12	8		< 0.008	
B-14	8		< 0.008	

Table 36

BLANK CONCENTRATIONS FOR DISSOLVED MOLYBDENUM

THE RANGE REPRESENTS THE
ONE SIGMA LEVEL

SAMPLE	NUMBER	MINIMUM	BEST VALUE	MAXIMUM
B-3B	1		< 0.03	
B-7B	1		< 0.03	
B-9B	1		< 0.10	
B-11A	2	0.13	0.14	0.15
B-5A	2		< 0.03	
B-7A	2		< 0.04	
B-11B	3		< 0.03	
B-3B	3		< 0.03	
B-7B	3		< 0.04	
B-17A	4		< 0.03	
B-19A	4		< 0.04	
B-21A	4		< 0.04	
B-21B	5		< 0.04	
B-25B	5		< 0.02	
B-7B	5		< 0.03	
B-11B	6		< 0.05	
B-13B	6		< 0.03	
B-17B	6		< 0.04	
B-4A	7		< 0.03	
B-6A	7		< 0.03	
B-8A	7		< 0.03	
B-10A	8		< 0.05	
B-12A	8		< 0.03	
B-14A	8		< 0.05	

Table 37

BLANK CONCENTRATIONS FOR DISSOLVED NICKEL
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE
ONE SIGMA LEVEL

SAMPLE	NUMBER	MINIMUM	BEST VALUE	MAXIMUM
B-3	1	0.04	0.05	0.06
B-9	1	0.04	0.05	0.06
B-9	1	0.05	0.06	0.07
B-11	2	0.03	0.04	0.05
B-5	2	0.05	0.06	0.07
B-7	2	0.01	0.02	0.03
B-11	3	0.09	0.10	0.11
B-3	3	0.33	0.37	0.41
B-7	3	0.30	0.33	0.36
B-17	4	0.21	0.23	0.25
B-19	4	0.14	0.16	0.18
B-21	4	0.15	0.17	0.19
B-21	5	0.06	0.08	0.10
B-25	5	0.03	0.04	0.05
B-11	6	0.05	0.07	0.09
B-13	6	0.05	0.06	0.07
B-21	6	0.05	0.06	0.07
B-4	7	0.29	0.33	0.37
B-6	7	0.15	0.17	0.19
B-8	7	0.20	0.22	0.24
B-10	8	0.13	0.15	0.17
B-12	8	0.05	0.06	0.07
B-14	8	0.08	0.10	0.12

Table 38

BLANK CONCENTRATIONS FOE DISSOLVED LEAD (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE
ONE SIGMA LEVEL

SAMPLE NUMBER		MINIMUM	BEST VALUE	MAXIMUM
B-3	1	0.21	0.23	0.25
B-9	1	0.12	0.14	0.16
B-9	1	0.07	0.09	0.11
B-11	2	0.17	0.19	0.21
B-5	2	0.14	0.16	0.18
B-7	2	0.23	0.25	0.27
B-11	3	0.08	0.10	0.12
B-3	3	0.08	0.10	0.12
B-7	3	0.12	0.14	0.16
B-17	4	0.11	0.13	0.15
B-19	4	0.08	0.10	0.12
B-21	4	0.11	0.13	0.15
B-21	5	0.19	0.21	0.23
B-25	5	0.17	0.19	0.21
B-11	6	0.16	0.18	0.20
B-13	6	0.12	0.14	0.16
B-21	6	0.05	0.07	0.09
B-4	7	0.11	0.13	0.15
B-6	7	0.08	0.10	0.12
B-8	7	0.05	0.07	0.09
B-10	8	0.15	0.17	0.19
B-12	8	0.10	0.12	0.14
B-14	8	0.09	0.11	0.13

Table 39

BLANK CONCENTRATIONS FOR DISSOLVED SCANDIUM (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE
ONE SIGMA LEVEL

SAMPLE NUMBER		MINIMUM	BEST VALUE	MAXIMUM
B-3B	1	0.00013	0.00014	0.00015
B-7B	1	0.00011	0.00012	0.00013
B-9B	1	0.00018	0.00020	0.00022
B-11A	2	0.00013	0.00014	0.00015
B-5A	2	0.00011	0.00012	0.00013
B-7A	2	0.00006	0.00007	0.00008
B-11B	3	0.00007	0.00008	0.00009
B-3B	3	0.00009	0.00010	0.00011
B-7B	3	0.00007	0.00008	0.00009
B-17A	4	0.00004	0.00005	0.00006
B-19A	4	0.00013	0.00014	0.00015
B-21A	4	0.00008	0.00009	0.00010
B-21B	5	0.00018	0.00020	0.00022
B-25B	5	0.00012	0.00013	0.00014
B-7B	5	0.00006	0.00007	0.00008
B-11B	6	0.00010	0.00011	0.00012
B-13B	6	0.00010	0.00011	0.00012
B-17B	6	0.00014	0.00015	0.00016
B-4A	7	0.00014	0.00016	0.00018
B-6A	7	0.00014	0.00015	0.00016
B-8A	7	0.00009	0.00010	0.00011
B-10A	8	0.00009	0.00010	0.00011
B-12A	8	0.00007	0.00009	0.00011
B-14A	8	0.00015	0.00016	0.00017

Table 40

BLANK CONCENTRATIONS FOR DISSOLVED TIN
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE
ONE SIGMA LEVEL

SAMPLE NUMBER		MINIMUM	BEST VALUE	MAXIMUM
B-3B	1		< 0.20	
B-7B	1		< 0.20	
B-9B	1		< 0.30	
B-11A	2		< 0.30	
B-5A	2		< 0.40	
B-7A	2		< 0.30	
B-11B	3		< 0.30	
B-3B	3		< 0.30	
B-7B	3		< 0.30	
B-17A	4		< 0.40	
B-19A	4		< 0.40	
B-21A	4		< 0.40	
B-21B	5		< 0.50	
B-25B	5		< 0.30	
B-7B	5		< 0.40	
B-11B	6		< 0.30	
B-13B	6		< 0.30	
B-17B	6		< 0.40	
B-4A	7		< 0.70	
B-6A	7		< 0.20	
B-8A	7		< 0.40	
B-10A	8		< 0.60	
B-12A	8		< 0.40	
B-14A	8		< 0.40	

Table 41

BLANK CONCENTRATIONS FOR DISSOLVED THORIUM (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE
ONE SIGMA LEVEL

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
B-3B 1	0.00034	0.00042	0.00050
B-7B 1	0.00039	0.00047	0.00055
B-9B 1	0.00038	0.00050	0.00062
B-11A 2	0.00024	0.00036	0.00048
B-5A 2	0.00040	0.00050	0.00060
B-7A 2		< 0.00040	
B-11B 3	0.00050	0.00060	0.00070
B-3B 3	0.00410	0.00440	0.00470
B-7B 3	0.00040	0.00050	0.00060
B-17A 4		< 0.00050	
B-19A 4	0.00040	0.00050	0.00060
B-21A 4		< 0.00050	
B-21B 5		< 0.00070	
B-25B 5		< 0.00050	
B-7B 5		< 0.00050	
B-11B 6	0.00060	0.00080	0.00100
B-13B 6	0.00030	0.00040	0.00050
B-17B 6	0.00160	0.00170	0.00180
B-4A 7		< 0.00080	
B-6A 7		< 0.00060	
B-8A 7		< 0.00060	
B-10A 8	0.00030	0.00050	0.00070
B-12A 8		< 0.00060	
B-14A 8	0.00040	0.00060	0.00080

Table 42

BLANK CONCENTRATIONS FOR DISSOLVED URANIUM (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE
ONE SIGMA LEVEL

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
B-3B 1	0.0008	0.0013	0.0018
B-7B 1		< 0.0020	
B-9B 1		< 0.0060	
B-11A 2	0.0310	0.0340	0.0370
B-5A 2	0.0032	0.0037	0.0042
B-7A 2		< 0.0020	
B-11B 3		< 0.0020	
B-3B 3	0.0016	0.0022	0.0028
B-7B 3		< 0.0030	
B-17A 4	0.0044	0.0049	0.0054
B-19A 4		< 0.0030	
B-21A 4		< 0.0020	
B-21B 5		< 0.0030	
B-25B 5		< 0.0010	
B-7B 5		< 0.0020	
B-11B 6		< 0.0030	
B-13B 6		< 0.0020	
B-17B 6		< 0.0020	
B-4A 7	0.0013	0.0017	0.0021
B-6A 7		< 0.0020	
B-8A 7		< 0.0020	
B-10A 8		< 0.0030	
B-12A 8		< 0.0020	
B-14A 8		< 0.0030	

Table 43

BLANK CONCENTRATIONS FOR DISSOLVED ZINC
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE
ONE SIGMA LEVEL

SAMPLE NUMBER		MINIMUM	BEST VALUE	MAXIMUM
B-3B	1	0.56	0.59	0.62
B-7B	1	0.59	0.62	0.65
B-9B	1	0.46	0.48	0.50
B-11A	2	0.36	0.38	0.40
B-5A	2	1.19	1.25	1.31
B-7A	2	1.08	1.14	1.20
B-11B	3	0.75	0.79	0.83
B-3B	3	0.76	0.80	0.84
B-7B	3	0.78	0.82	0.86
B-17A	4	1.54	1.62	1.70
B-19A	4	1.07	1.13	1.19
B-21A	4	0.89	0.94	0.99
B-21B	5	1.04	1.10	1.16
B-25B	5	1.36	1.43	1.50
B-7B	5	0.76	0.80	0.84
B-11B	6	2.00	2.10	2.20
B-13B	6	1.14	1.20	1.26
B-17B	6	1.42	1.49	1.56
B-4A	7	0.86	0.91	0.96
B-6A	7	1.07	1.13	1.19
B-8A	7	3.80	4.00	4.20
B-10A	8	3.30	3.50	3.70
B-12A	8	2.10	2.20	2.30
B-14A	8	3.40	3.60	3.80

Table 44

BLANK CONCENTRATIONS FOR PARTICULATE CADMIUM
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE
ONE SIGMA LEVEL

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
B-#9		< 0.001	
B-#6		< 0.001	
B-#22		< 0.001	
B-#21		< 0.001	
B-#20		< 0.001	
B-#19		< 0.001	
B-#12		< 0.001	
B-#11		< 0.001	
B-#10		< 0.001	

Table 45

BLANK CONCENTRATIONS FOR PARTICULATE CERIUM (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE ONE SIGMA LEVEL

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
AM-2		< 0.0080	
BLANK-13		< 0.0040	
BLANK-14		< 0.0030	
BLANK-15		< 0.0040	
BLANK-16		< 0.0050	
BLANK-17	0.0050	0.0060	0.0070
BLANK-18		< 0.0070	
BLANK-2	0.0300	0.0320	0.0340
BLANK-25	0.0040	0.0050	0.0060
BLANK-26		< 0.0020	
BLANK-5		< 0.0080	
BLANK-8		< 0.0020	
BLK-1		< 0.0080	
BLK-7		< 0.0070	
LPE		< 0.0020	
LPE		< 0.0030	
LPE-1		< 0.0060	
LPE-2	0.0013	0.0014	0.0015
MP-10		< 0.0050	
MP-5+MP-9		< 0.0200	

Table 46

BLANK CONCENTRATIONS FOR PARTICULATE COBALT (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE
ONE SIGMA LEVEL

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
AM-2		< 0.0040	
BLANK-13		< 0.0060	
BLANK-14	0.0020	0.0026	0.0032
BLANK-15		< 0.0010	
BLANK-16		< 0.0050	
BLANK-17	0.0010	0.0016	0.0022
BLANK-18	0.0042	0.0050	0.0058
BLANK-2	0.0130	0.0140	0.0150
BLANK-25	0.0018	0.0028	0.0038
BLANK-26		< 0.0010	
BLANK-5		< 0.0050	
BLANK-8		< 0.0030	
BLK-1		< 0.0040	
BLK-7		< 0.0060	
LPE		< 0.0010	
LPE		< 0.0060	
LPE-1	0.0008	0.0012	0.0016
LPE-2	0.0003	0.0005	0.0007
MP-10	0.0020	0.0030	0.0040
MP-5+MP-9		< 0.0040	

Table 47

BLANK CONCENTRATIONS FOR PARTICULATE CHROMIUM (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE ONE SIGMA LEVEL

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
AM-2	0.740	0.780	0.820
BLANK-13	2.170	2.290	2.410
BLANK-14	0.600	0.630	0.660
BLANK-15	0.680	0.720	0.760
BLANK-16	0.230	0.240	0.250
BLANK-17	1.260	1.330	1.400
BLANK-18	0.400	0.420	0.440
BLANK-2	0.270	0.280	0.290
BLANK-25	1.130	1.190	1.250
BLANK-26	0.440	0.460	0.480
BLANK-5	2.260	2.380	2.500
BLANK-8	0.360	0.380	0.400
BLK-1	0.710	0.750	0.790
BLK-7	1.790	1.880	1.970
LPE	0.064	0.067	0.070
LPE	0.066	0.070	0.074
LPE-1	0.086	0.092	0.098
LPE-2	0.070	0.074	0.078
MP-10	0.220	0.230	0.240
MP-5+MP-9	0.450	0.470	0.490

Table 48

BLANK CONCENTRATIONS FOR PARTICULATE COPPER (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE
ONE SIGMA LEVEL

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
B-#9	0.17	0.20	0.23
B-#6	0.55	0.63	0.71
B-#22	0.49	0.55	0.61
B-#21	0.34	0.38	0.42
B-#20	0.57	0.64	0.71
B-#19	0.64	0.71	0.78
B-#12	0.57	0.64	0.71
B-#11	0.30	0.34	0.38
B-#10	0.25	0.28	0.31

Table 49

BLANK CONCENTRATIONS FOR PARTICULATE IRON
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE
ONE SIGMA LEVEL

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
AM-2		< 3.00	
BLANK-13	0.90	1.10	1.30
BLANK-14	1.40	1.55	1.70
BLANK-15		< 0.80	
BLANK-16		< 3.00	
BLANK-17	1.43	1.65	1.87
BLANK-18	0.30	0.50	0.70
BLANK-2	1.80	1.90	2.00
BLANK-25	3.30	3.50	3.70
BLANK-26	0.40	0.50	0.60
BLANK-5		< 3.00	
BLANK-8	0.30	0.50	0.70
BLK-1		< 2.00	
BLK-7		< 2.00	
LPE		< 0.60	
LPE		< 0.70	
LPE-1		< 0.60	
LPE-2	0.70	0.75	0.80
MP-10		< 2.00	
MP-5+MP-9		< 2.00	

Table 50

BLANK CONCENTRATIONS FOR PARTICULATE MANGANESE
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE
ONE SIGMA LEVEL

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
B-#9		< 0.010	
B-#6	0.052	0.060	0.068
B-#22		< 0.010	
B-#21		< 0.010	
B-#20		< 0.010	
B-#19	0.030	0.040	0.050
B-#12		< 0.010	
B-#11		< 0.010	
B-#10		< 0.010	

Table 51

BLANK CONCENTRATIONS FOR PARTICULATE MOLYBDENUM (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE
ONE SIGMA LEVEL

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
AM-2		<0.0060	
BLANK-13		<0.0090	
BLANK-14		<0.0500	
BLANK-15		<0.0200	
BLANK-16		<0.0050	
BLANK-17		<0.0800	
BLANK-18		<0.0040	
BLANK-2		<0.0200	
BLANK-25		<0.1000	
BLANK-26		<0.0200	
BLANK-5		<0.0060	
BLANK-8		<0.0200	
BLK-1		<0.0070	
BLK-7		<0.0080	
LPE		<0.0002	
LPE		<0.0070	
LPE-1		<0.0200	
LPE-2		<0.0100	
MP-10		<0.0040	
MP-5+MP-9		<0.0300	

Table 52

BLANK CONCENTRATIONS FOR PARTICULATE NICKEL
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE
ONE SIGMA LEVEL

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
B-#9		< 0.02	
B-#6		< 0.02	
B-#22		< 0.02	
B-#21	0.06	0.07	0.08
B-#20		< 0.02	
B-#19	0.08	0.09	0.10
B-#12		< 0.02	
B-#11		< 0.02	
B-#10		< 0.02	

Table 53

BLANK CONCENTRATIONS FOR PARTICULATE LEAD (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE
ONE SIGMA LEVEL

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
B-#9	0.01	0.02	0.03
B-#6	0.03	0.04	0.05
B-#22		< 0.01	
B-#21		< 0.01	
B-#20		< 0.01	
B-#19		< 0.01	
B-#12		< 0.01	
B-#11	0.03	0.04	0.05
B-#10	0.02	0.03	0.04

Table 54

BLANK CONCENTRATIONS FOR PARTICULATE SCANDIUM (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE ONE SIGMA LEVEL

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
AM-2		<0.00030	
BLANK-13	0.00011	0.00013	0.00015
BLANK-14	0.00032	0.00034	0.00036
BLANK-15		<0.00009	
BLANK-16		<0.00020	
BLANK-17	0.00049	0.00053	0.00057
BLANK-18		<0.00005	
BLANK-2	0.00030	0.00040	0.00050
BLANK-25	0.00069	0.00076	0.00083
BLANK-26	0.00007	0.00009	0.00011
BLANK-5		<0.00040	
BLANK-8	0.00003	0.00004	0.00005
BLK-1		<0.00020	
BLK-7		<0.00020	
LPE		<0.00005	
LPE		<0.00007	
LPE-1		<0.00001	
LPE-2	0.00020	0.00021	0.00022
MP-10		<0.00020	
MP-5+MP-9	0.00015	0.00020	0.00025

Table 55

BLANK CONCENTRATIONS FOR PARTICULATE TIN (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE ONE SIGMA LEVEL

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
AM-2		< 0.30	
BLANK-13		< 0.20	
BLANK-14		< 0.20	
BLANK-15		< 0.20	
BLANK-16		< 0.30	
BLANK-17		< 0.20	
BLANK-18		< 0.30	
BLANK-2		< 0.20	
BLANK-25		< 0.30	
BLANK-26		< 0.30	
BLANK-5		< 0.30	
BLANK-8		< 0.20	
BLK-1		< 0.30	
BLK-7		< 0.30	
LPE		< 0.09	
LPE		< 0.10	
LPE-1		< 0.50	
LPE-2		< 0.04	
MP-10		< 0.20	
MP-5+MP-9		< 0.90	

Table 56

BLANK CONCENTRATIONS FOR PARTICULATE THORIUM (IN NANOGRAMS/MILLILITER)

SAMPLE NUMBER	MINIMUM	THE RANGE REPRESENTS THE ONE SIGMA LEVEL BEST VALUE	MAXIMUM
AM-2		<0.00200	
BLANK-13		<0.00060	
BLANK-14		<0.00050	
BLANK-15		<0.00050	
BLANK-16		<0.00100	
BLANK-17		<0.00050	
BLANK-18		<0.00040	
BLANK-2		<0.00040	
BLANK-25	0.00100	0.00110	0.00120
BLANK-26		<0.00020	
BLANK-5		<0.00200	
BLANK-8		<0.00030	
BLK-1		<0.00200	
BLK-7		<0.00010	
LPE		<0.00050	
LPE		<0.00060	
LPE-1		<0.00070	
LPE-2	0.00020	0.00024	0.00028
MP-10		<0.00010	
MP-5+MP-9		<0.00200	

Table 57

BLANK CONCENTRATIONS FOR PARTICULATE URANIUM (IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE
ONE SIGMA LEVEL

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
AM-2		<0.00040	
BLANK-13		<0.00007	
BLANK-14		<0.00500	
BLANK-15		<0.00200	
BLANK-16		<0.00030	
BLANK-17		<0.00800	
BLANK-18		<0.00030	
BLANK-2		<0.00300	
BLANK-25		<0.01000	
BLANK-26		<0.00100	
BLANK-5		<0.00100	
BLANK-8		<0.00200	
BLK-1		<0.00100	
BLK-7		<0.00060	
LPE		<0.00020	
LPE		<0.00070	
LPE-1		<0.00200	
LPE-2		<0.00100	
MP-10		<0.00030	
MP-5+MP-9		<0.00200	

Table 58

BLANK CONCENTRATIONS FOR PARTICULATE ZINC
(IN NANOGRAMS/MILLILITER)

THE RANGE REPRESENTS THE
ONE SIGMA LEVEL

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
AM-2		< 0.300	
BLANK-13	0.470	0.500	0.530
BLANK-14	0.280	0.310	0.340
BLANK-15	0.120	0.140	0.160
BLANK-16		< 0.300	
BLANK-17	0.380	0.420	0.460
BLANK-18	0.890	0.940	0.990
BLANK-2	0.110	0.130	0.150
BLANK-25	0.480	0.530	0.580
BLANK-26	1.500	1.600	1.700
BLANK-5	0.460	0.560	0.660
BLANK-8	0.100	0.110	0.120
BLK-1		< 0.200	
BLK-7	0.240	0.290	0.340
LPE		< 0.040	
LPE		< 0.060	
LPE-1		< 0.040	
LPE-2	0.010	0.013	0.016
MP-10		< 0.200	
MP-5+MP-9	•	•	•

Table 59

CRUSTAL ENRICHMENT FACTORS FOR PARTICULATE CADMIUM RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102	3.496	5.537	7.869
11101	15.113	20.419	26.837
11100	1.676	3.630	6.040
11099	8.684	12.923	18.097
11098	12.120	18.150	25.993
11097	16.740	24.282	33.612
11096	2.992	5.294	8.159
11095	3.937	6.534	9.824
11094	10.124	14.603	20.153
11093	18.496	24.956	32.996
11092	6.593	11.020	16.358
11091	3.373	5.445	7.913
11090	0.898	2.836	5.183
11089	4.330	8.391	13.296
11088	3.083	9.723	17.731
11087	3.911	7.090	10.991
11086	0.000	8.007	26.446
11085		<	
11084		<	
11083	5.063	15.707	28.086
11082	9.850	31.414	58.065
11081		<	
11080	76.070	137.501	212.430
11079	24.839	53.383	87.995
11078	16.277	37.813	64.612
11077	6.776	17.016	29.659
11076	0.248	13.613	29.881
11075		<	
11074	49.237	105.729	174.101
11073	27.275	49.321	76.234
11072	35.708	74.650	124.866
11071	24.978	50.307	80.356
11070	0.491	26.956	59.107
11069	0.218	11.837	25.621
11068	0.195	10.471	22.423
11067	5.599	13.810	23.550
11066	33.522	72.601	120.803
11065		<	
11064		<	
11063	4.715	10.083	16.524
11062		<	
11061	8.043	13.068	19.137
11060		<	
11059		<	
11058	0.000	20.942	68.155
11057		<	
11056		<	
11055		<	
11054		<	
11053		<	
11052		<	

Table 59 continued

CRUSTAL ENRICHMENT FACTORS FOR PARTICULATE CADMIUM RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051		<	
11050		<	
11049		<	
11048	262.272	348.230	451.432
11047	12.838	20.019	28.810
11046	22.514	71.645	132.079
11045	13.043	19.208	26.686
11044		<	
11043	5.017	7.623	10.771
11042		<	
11041		<	
11040		<	
11039		<	
11038		<	
11037		<	
11036	632.364	855.650	1135.260
11035		<	
11034		<	
11033		<	
11032		<	
11031		<	
11030		<	
11029		<	
11028		<	
11027		<	
11026		<	
11025		<	
11024		<	
11023		<	
11022		<	
11021	33.387	54.090	78.931
11020	0.000	6.188	20.106
11019	6.588	15.598	26.657
11018		<	
11017	0.000	1.184	3.903
11016		<	
11015		<	
11014		<	
11013		<	
11012		<	
11011	0.031	1.723	3.788
11010		<	
11009	0.119	6.482	14.156
11008		<	
11007		<	
11006		<	
11005	0.142	0.454	0.842
11004		<	
11003	3.057	6.560	10.794
11002		<	
11001	5.526	9.864	15.010

Table 60

CRUSTAL ENRICHMENT FACTORS FOR PARTICULATE CERIUM RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102	1.04	1.23	1.45
11101	1.02	1.23	1.49
11100	1.28	1.56	1.90
11099	1.28	1.57	1.92
11098	1.27	1.56	1.93
11097	1.19	1.51	1.91
11096	1.16	1.42	1.74
11095	1.21	1.49	1.86
11094	1.32	1.60	1.94
11093	1.31	1.59	1.94
11092	1.11	1.35	1.64
11091	0.96	1.12	1.32
11090	0.90	1.09	1.32
11089	0.91	1.10	1.32
11088	0.94	1.16	1.42
11087	0.88	1.09	1.34
11086	0.89	1.09	1.33
11085	1.30	1.59	1.94
11084	0.92	1.11	1.34
11083	0.94	1.12	1.33
11082	0.91	1.12	1.38
11081	0.95	1.13	1.35
11080	0.95	1.15	1.40
11079	0.92	1.15	1.43
11078	0.91	1.14	1.43
11077	0.91	1.13	1.41
11076	1.01	1.24	1.52
11075	0.99	1.20	1.44
11074	1.04	1.25	1.50
11073	1.37	1.66	2.02
11072	0.96	1.20	1.51
11071	1.01	1.18	1.37
11070	1.00	1.24	1.53
11069	1.00	1.19	1.43
11068	1.00	1.18	1.40
11067	0.97	1.16	1.39
11066	0.97	1.37	1.86
11065	1.04	1.27	1.54
11064	0.90	1.16	1.47
11063	0.95	1.14	1.37
11062	0.89	1.11	1.38
11061	0.90	1.11	1.35
11060	1.02	1.27	1.58
11059	0.96	1.22	1.54
11058	0.98	1.23	1.54
11057	1.06	1.27	1.50
11056	0.95	1.14	1.38
11055	1.00	1.20	1.43
11054	0.91	1.12	1.38
11053	0.95	1.17	1.44
11052	0.89	1.13	1.42

Table 60 continued

CRUSTAL ENRICHMENT FACTORS FOR PARTICULATE CERIUM RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051	0.97	1.21	1.48
11050	1.00	1.24	1.52
11049	0.94	1.17	1.45
11048	1.00	1.26	1.57
11047	0.96	1.17	1.42
11046	1.13	1.38	1.68
11045	0.98	1.19	1.44
11044	1.03	1.29	1.59
11043	1.04	1.25	1.51
11042	1.14	1.42	1.77
11041	1.02	1.27	1.58
11040	1.11	1.37	1.68
11039	1.00	1.22	1.50
11038	0.91	1.18	1.50
11037	1.00	1.27	1.61
11036		<	
11035	1.07	1.29	1.55
11034	1.09	1.42	1.79
11033	1.12	1.33	1.57
11032	1.17	1.49	1.86
11031	0.94	1.18	1.47
11030	1.05	1.30	1.59
11029	1.00	1.21	1.46
11028	1.07	1.38	1.75
11027	1.04	1.26	1.53
11026	1.05	1.30	1.59
11025	0.99	1.23	1.51
11024	1.03	1.27	1.57
11023	1.11	1.32	1.56
11022	0.99	1.32	1.73
11021	1.02	1.24	1.49
11020	1.05	1.26	1.52
11019	0.99	1.21	1.47
11018	1.05	1.27	1.53
11017	1.00	1.23	1.52
11016	0.71	1.13	1.63
11015	1.09	1.32	1.59
11014	0.85	1.14	1.51
11013	1.04	1.26	1.55
11012	1.04	1.28	1.59
11011	1.06	1.28	1.55
11010	1.14	1.40	1.72
11009	0.94	1.20	1.52
11008	1.04	1.27	1.54
11007	1.05	1.24	1.49
11006	0.96	1.18	1.44
11005	1.01	1.24	1.53
11004	0.99	1.22	1.50
11003	1.05	1.28	1.56
11002	1.14	1.42	1.76
11001	1.05	1.24	1.48

Table 61

CRUSTAL ENRICHMENT FACTORS FOR PARTICULATE COBALT RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102	2.04	2.41	2.83
11101	1.96	2.37	2.86
11100	3.88	4.74	5.81
11099	3.97	4.80	5.81
11098	3.52	4.43	5.63
11097	3.51	4.32	5.32
11096	2.29	2.83	3.51
11095	2.36	2.92	3.62
11094	4.03	4.88	5.93
11093	4.10	4.97	6.05
11092	2.34	2.89	3.55
11091	2.56	3.09	3.71
11090	2.45	3.00	3.66
11089	2.49	3.04	3.70
11088	2.16	2.61	3.15
11087	2.15	2.61	3.18
11086	2.93	3.64	4.51
11085	1.72	2.17	2.72
11084	2.39	2.89	3.49
11083	2.30	2.74	3.25
11082	3.17	3.86	4.71
11081	2.58	3.08	3.67
11080	3.12	3.89	4.83
11079	3.45	4.23	5.18
11078	1.23	1.49	1.82
11077	1.17	1.46	1.81
11076	1.92	2.45	3.10
11075	2.30	2.77	3.33
11074	2.90	3.62	4.50
11073	1.16	1.44	1.78
11072	1.44	1.84	2.36
11071	1.45	1.78	2.16
11070	2.64	3.35	4.21
11069	1.83	2.18	2.60
11068	1.47	1.84	2.28
11067	1.39	1.67	2.01
11066	1.72	3.42	5.52
11065	1.13	1.68	2.32
11064	0.31	0.78	1.34
11063	0.52	0.69	0.90
11062	0.89	1.13	1.44
11061	0.97	1.18	1.42
11060	3.58	4.84	6.42
11059	4.19	5.29	6.61
11058	2.81	3.77	4.92
11057	1.33	1.58	1.88
11056	2.71	3.62	4.71
11055	1.55	1.88	2.29
11054	0.93	1.17	1.46
11053	0.96	1.17	1.42
11052	0.76	1.01	1.33

Table 61 continued

CRUSTAL ENRICHMENT FACTORS FOR PARTICULATE COBALT RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051	1.15	1.39	1.66
11050	0.96	1.20	1.48
11049	1.05	1.30	1.60
11048	1.37	1.66	2.00
11047	0.97	1.18	1.45
11046	3.91	5.12	6.60
11045	1.04	1.27	1.54
11044	1.46	1.79	2.18
11043	1.71	2.05	2.47
11042	5.65	7.23	9.23
11041	1.05	1.30	1.60
11040	7.65	9.33	11.34
11039	1.04	1.27	1.54
11038	4.61	5.91	7.48
11037	1.09	1.37	1.70
11036	8.17	13.00	19.05
11035	1.17	1.53	1.94
11034	6.80	8.05	9.47
11033	1.52	1.87	2.28
11032	4.88	6.67	8.77
11031	4.60	5.83	7.33
11030	1.83	2.49	3.26
11029	0.92	1.13	1.38
11028	2.90	3.68	4.64
11027	1.44	1.79	2.23
11026	1.59	2.03	2.54
11025	0.97	1.24	1.57
11024	1.89	2.59	3.45
11023	1.43	1.78	2.21
11022	1.40	2.23	3.28
11021	1.02	1.24	1.49
11020	1.71	2.17	2.73
11019	1.14	1.40	1.72
11018	1.37	1.66	2.02
11017	1.46	1.79	2.19
11016	4.26	6.11	8.34
11015	1.05	1.34	1.69
11014	2.35	3.37	4.64
11013	1.51	1.89	2.36
11012	1.53	2.08	2.78
11011	0.97	1.18	1.44
11010	1.54	2.15	2.90
11009	1.40	1.86	2.41
11008	1.30	1.59	1.92
11007	1.25	1.56	1.92
11006	0.95	1.21	1.53
11005	1.08	1.32	1.63
11004	1.16	1.40	1.71
11003	1.21	1.49	1.83
11002	1.94	2.78	3.78
11001	1.09	1.32	1.59

Table 62

CRUSTAL ENRICHMENT FACTORS OF PARTICULATE CHROMIUM AS COMPARED TO SCANDIUM (WEDEPOHL)

		THE RANGE REPRESENTS AT LEAST THE 90% CONFIDENCE LIMITS	
SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102	1.11	1.48	1.82
11101	0.99	1.44	1.90
11100	0.96	1.64	2.15
11099	0.96	1.61	2.09
11098	1.15	1.70	2.23
11097	1.09	1.65	2.20
11096	1.22	1.77	2.34
11095	1.35	1.95	2.60
11094	1.16	1.58	2.01
11093	1.18	1.61	2.05
11092	1.29	2.26	3.17
11091	1.01	1.50	1.96
11090	0.58	1.33	1.89
11089	0.52	1.26	1.81
11088	0.37	1.55	2.37
11087	0.78	1.46	2.02
11086	0.00	1.65	4.56
11085	0.00	1.61	4.64
11084	0.00	1.91	4.06
11083	0.00	1.62	3.47
11082	0.00	2.46	7.35
11081	0.00	2.36	4.13
11080	0.00	1.82	14.78
11079	0.00	2.75	15.38
11078	0.00	1.33	4.59
11077	0.00	0.75	3.11
11076	0.00	0.90	7.31
11075	0.00	4.75	10.74
11074	0.00	3.11	15.65
11073	0.00	0.00	8.64
11072	0.00	1.68	6.12
11071	0.00	1.52	4.48
11070	0.00	0.00	11.33
11069	0.00	2.09	7.69
11068	0.00	0.15	4.72
11067	0.00	1.25	3.24
11066	0.00	0.00	15.09
11065	0.00	0.88	5.90
11064	0.00	0.71	3.78
11063	0.00	0.80	2.08
11062	0.25	1.01	1.81
11061	0.00	0.00	0.93
11060	0.00	0.00	14.19
11059	0.00	0.00	12.54
11058	0.00	4.00	23.65
11057	0.00	0.57	4.99
11056	0.00	0.14	8.68
11055	0.00	1.90	5.48
11054	0.00	0.60	2.51
11053	0.00	0.86	2.12
11052	0.00	1.43	4.12

Table 62 continued

CRUSTAL ENRICHMENT FACTORS OF PARTICULATE CHROMIUM AS COMPARED TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051	0.00	0.58	3.22
11050	0.00	0.18	1.77
11049	0.00	0.52	2.16
11048	0.00	0.00	2.29
11047	0.00	0.26	1.58
11046	0.00	0.00	5.84
11045	0.00	0.00	0.94
11044	0.00	0.00	1.63
11043	0.00	0.46	1.91
11042	0.00	0.00	15.61
11041	0.00	0.00	1.22
11040	0.00	0.00	20.29
11039	0.84	2.16	3.45
11038	0.00	0.00	5.04
11037	0.00	0.00	2.30
11036	0.00	0.00	9.29
11035	0.00	0.00	1.10
11034	0.00	0.00	35.27
11033	0.00	1.21	5.68
11032	0.00	7.35	42.98
11031	0.00	2.22	11.19
11030	0.00	5.83	12.42
11029	0.09	1.48	2.77
11028	0.00	3.05	10.35
11027	0.00	0.39	3.08
11026	0.00	0.00	0.21
11025	0.00	3.06	6.30
11024	0.00	3.11	12.85
11023	0.00	1.71	3.84
11022	0.00	0.88	4.78
11021	0.55	1.83	3.04
11020	0.00	4.18	12.69
11019	0.00	0.77	2.74
11018	0.00	1.33	2.98
11017	0.00	1.46	3.29
11016	0.00	1.90	21.25
11015	0.00	1.05	3.31
11014	0.00	2.56	7.13
11013	0.00	0.82	4.72
11012	0.00	2.56	7.13
11011	0.00	0.58	1.48
11010	0.00	0.00	6.56
11009	0.00	2.67	6.17
11008	0.00	1.36	4.25
11007	0.00	1.08	3.15
11006	0.32	1.02	1.69
11005	0.70	1.15	1.64
11004	0.00	0.64	2.01
11003	0.00	1.40	3.76
11002	0.00	0.10	5.85
11001	0.00	1.42	3.50

Table 63

CRUSTAL ENRICHMENT FACTORS FOR PARTICULATE COPPER RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102	0.14	0.78	1.45
11101	0.26	0.89	1.58
11100	1.17	2.63	4.20
11099	0.85	2.21	3.65
11098	0.79	2.03	3.51
11097	0.85	2.13	3.62
11096	0.28	1.19	2.25
11095	0.30	1.29	2.45
11094	0.69	1.93	3.41
11093	1.45	2.81	4.42
11092	0.00	1.34	3.24
11091	0.18	1.03	1.94
11090	0.00	1.01	2.54
11089	0.00	0.84	2.33
11088	0.00	2.38	5.19
11087	0.00	0.99	2.24
11086	0.00	0.00	7.73
11085	0.00	0.00	5.22
11084	0.00	0.00	2.96
11083	0.00	0.00	2.78
11082	0.00	0.00	6.32
11081	0.00	0.00	5.61
11080	0.00	0.00	7.49
11079	0.00	0.00	4.78
11078	0.00	0.00	1.62
11077	0.00	0.00	1.42
11076	0.00	0.00	3.95
11075	0.00	0.00	4.32
11074	0.00	0.44	17.14
11073	0.00	0.00	9.48
11072	0.00	0.00	3.18
11071	0.00	0.00	3.12
11070	0.00	0.00	11.42
11069	0.00	0.00	6.03
11068	0.00	0.35	6.83
11067	0.00	0.66	3.34
11066	0.00	0.00	23.11
11065	0.00	2.36	9.74
11064	0.00	1.30	5.77
11063	0.00	0.84	2.71
11062	0.00	0.00	0.38
11061	0.00	1.38	3.25
11060	0.00	9.42	45.68
11059	0.00	0.00	25.92
11058	0.00	0.00	25.48
11057	0.00	2.43	8.96
11056	0.00	0.00	5.91
11055	0.00	0.81	5.33
11054	0.00	0.52	3.08
11053	0.00	0.08	1.55
11052	0.00	0.17	3.49

Table 63 continued

CRUSTAL ENRICHMENT FACTORS FOR PARTICULATE COPPER RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051	0.00	2.28	6.46
11050	0.00	0.00	1.57
11049	0.00	0.00	1.44
11048	0.00	0.00	1.24
11047	0.00	0.23	2.00
11046	0.00	0.00	17.93
11045	0.00	1.17	2.88
11044	0.00	0.00	2.98
11043	0.00	0.47	2.40
11042	0.00	0.00	29.78
11041	0.00	0.00	3.87
11040	0.00	0.00	36.67
11039	0.00	0.68	2.02
11038	0.00	0.00	17.34
11037	0.00	0.00	3.42
11036	0.00	0.00	40.82
11035	0.00	0.00	2.78
11034	0.00	0.00	21.35
11033	0.00	0.00	5.22
11032	0.00	13.89	64.58
11031	0.00	0.00	9.74
11030	0.00	4.14	12.87
11029	0.00	0.39	1.87
11028	0.00	2.15	12.10
11027	0.00	1.21	4.90
11026	0.00	0.00	6.73
11025	0.00	0.58	4.47
11024	0.00	0.00	11.67
11023	0.00	0.00	1.53
11022	0.00	0.93	6.55
11021	0.00	0.66	2.08
11020	0.00	0.00	9.21
11019	0.00	0.00	2.14
11018	0.00	0.33	2.33
11017	0.00	0.24	2.33
11016	0.00	0.00	19.03
11015	0.00	0.74	3.82
11014	0.00	6.55	15.40
11013	0.00	0.00	5.01
11012	0.00	0.00	5.36
11011	0.00	1.41	3.01
11010	0.00	0.00	10.72
11009	0.00	0.43	4.55
11008	0.00	0.00	3.44
11007	0.00	0.23	3.07
11006	0.32	1.20	2.15
11005	0.60	1.42	2.39
11004	0.00	0.66	2.53
11003	0.00	0.00	0.98
11002	0.00	0.00	7.91
11001	0.00	0.26	2.91

Table 64

CRUSTAL ENRICHMENT FACTORS OF PARTICULATE IRON RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102	0.93	1.12	1.31
11101	0.92	1.14	1.38
11100	1.07	1.37	1.70
11099	1.09	1.38	1.69
11098	1.04	1.33	1.68
11097	1.05	1.30	1.60
11096	1.01	1.27	1.58
11095	1.03	1.30	1.61
11094	1.07	1.33	1.63
11093	1.08	1.35	1.66
11092	1.08	1.36	1.66
11091	1.01	1.24	1.49
11090	0.93	1.15	1.39
11089	0.94	1.16	1.40
11088	0.96	1.18	1.40
11087	0.95	1.19	1.47
11086	0.86	1.14	1.37
11085	1.51	1.97	2.39
11084	0.85	1.10	1.31
11083	0.88	1.14	1.36
11082	0.85	1.19	1.46
11081	1.12	1.41	1.67
11080	0.79	1.20	1.50
11079	0.91	1.32	1.63
11078	0.77	1.00	1.23
11077	0.80	1.02	1.24
11076	1.05	1.36	1.64
11075	1.27	1.61	1.93
11074	0.77	1.15	1.44
11073	3.09	3.95	4.83
11072	0.75	1.01	1.27
11071	0.81	1.03	1.24
11070	0.82	1.14	1.34
11069	1.28	1.65	1.99
11068	0.91	1.17	1.40
11067	1.02	1.26	1.50
11066	0.66	1.16	1.53
11065	1.46	1.85	2.21
11064	0.69	0.94	1.18
11063	0.75	0.92	1.09
11062	0.71	0.91	1.14
11061	0.76	0.92	1.08
11060	0.81	1.34	1.68
11059	1.02	1.48	1.77
11058	0.90	1.34	1.60
11057	1.30	1.64	1.94
11056	0.88	1.20	1.45
11055	0.99	1.27	1.54
11054	0.67	0.87	1.08
11053	0.71	0.87	1.04
11052	0.77	1.04	1.34

Table 64 continued

CRUSTAL ENRICHMENT FACTORS OF PARTICULATE IRON RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051	0.82	1.03	1.23
11050	0.77	0.98	1.19
11049	0.82	1.03	1.25
11048	0.86	1.09	1.32
11047	0.80	1.02	1.26
11046	0.63	1.11	1.39
11045	0.87	1.07	1.29
11044	0.82	1.04	1.25
11043	0.76	0.98	1.22
11042	1.07	1.66	2.06
11041	1.11	1.40	1.69
11040	0.93	1.51	1.83
11039	1.03	1.26	1.51
11038	0.97	1.46	1.83
11037	1.22	1.54	1.87
11036	0.67	1.92	2.91
11035	1.16	1.48	1.76
11034	1.08	1.87	2.20
11033	1.18	1.47	1.73
11032	0.98	1.53	1.84
11031	1.39	1.81	2.18
11030	1.17	1.53	1.86
11029	1.06	1.31	1.58
11028	1.03	1.35	1.65
11027	0.97	1.23	1.50
11026	0.99	1.29	1.56
11025	1.00	1.27	1.53
11024	1.01	1.35	1.63
11023	1.09	1.34	1.59
11022	0.96	1.24	1.54
11021	1.03	1.31	1.61
11020	1.09	1.42	1.71
11019	0.98	1.28	1.60
11018	1.02	1.27	1.53
11017	1.00	1.27	1.57
11016	0.85	1.44	1.86
11015	0.99	1.26	1.53
11014	1.02	1.36	1.67
11013	1.02	1.34	1.67
11012	0.98	1.29	1.60
11011	1.01	1.23	1.47
11010	1.03	1.40	1.74
11009	0.99	1.26	1.53
11008	1.03	1.31	1.56
11007	1.02	1.32	1.62
11006	0.94	1.16	1.41
11005	1.00	1.24	1.53
11004	0.97	1.20	1.46
11003	1.00	1.25	1.52
11002	1.18	1.53	1.85
11001	1.13	1.38	1.63

Table 65

CRUSTAL ENRICHMENT FACTORS FOR PARTICULATE MANGANESE RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102	2.9	3.9	5.0
11101	3.0	4.0	5.3
11100	11.4	15.7	20.9
11099	12.1	16.2	21.3
11098	7.6	10.4	14.0
11097	7.4	9.7	12.6
11096	5.2	6.8	8.9
11095	5.5	7.3	9.5
11094	8.0	9.9	12.3
11093	10.3	12.8	15.8
11092	4.6	6.2	8.1
11091	4.0	5.0	6.3
11090	4.5	6.0	8.0
11089	4.7	6.4	8.4
11088	6.6	8.8	11.5
11087	5.6	7.6	9.9
11086	22.1	30.3	40.4
11085	2.6	3.6	4.7
11084	16.7	22.5	29.3
11083	17.2	22.9	29.6
11082	37.2	51.3	68.7
11081	19.4	25.9	33.3
11080	26.4	36.1	47.8
11079	27.8	37.7	49.7
11078	5.2	7.2	9.6
11077	6.1	8.3	11.2
11076	29.1	39.5	52.1
11075	26.0	34.4	44.3
11074	17.0	23.2	30.6
11073	1.1	1.7	2.5
11072	7.0	9.9	13.6
11071	6.9	9.1	11.7
11070	9.3	12.9	17.2
11069	6.4	8.4	10.8
11068	10.8	14.3	18.4
11067	8.1	10.9	14.2
11066	12.0	16.8	22.8
11065	16.8	22.6	29.4
11064	6.6	9.0	12.0
11063	3.9	5.1	6.6
11062	1.4	1.9	2.6
11061	6.5	8.3	10.5
11060	33.7	46.2	61.8
11059	53.3	72.1	94.7
11058	28.0	37.6	49.2
11057	6.6	8.7	11.2
11056	24.2	32.8	43.2
11055	8.4	11.4	15.1
11054	2.7	3.7	5.0
11053	2.1	2.8	3.7
11052	4.6	6.3	8.4

Table 65 continued

CRUSTAL ENRICHMENT FACTORS FOR PARTICULATE MANGANESE RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051	6.0	7.9	10.2
11050	3.7	5.0	6.6
11049	4.2	5.8	7.6
11048	8.1	10.9	14.3
11047	3.4	4.6	6.1
11046	30.6	41.9	55.8
11045	4.2	5.6	7.4
11044	8.6	11.7	15.3
11043	4.0	5.4	7.1
11042	28.7	39.9	53.9
11041	3.2	4.4	5.8
11040	37.3	50.9	67.0
11039	1.1	1.5	2.0
11038	29.9	40.4	53.2
11037	2.2	3.0	4.1
11036	40.8	56.4	75.9
11035	5.3	7.1	9.1
11034	59.6	79.6	102.5
11033	4.3	5.8	7.6
11032	40.8	54.4	70.2
11031	15.5	20.7	27.0
11030	7.8	10.5	13.6
11029	1.4	1.9	2.5
11028	11.4	15.9	21.3
11027	5.9	8.1	10.9
11026	7.5	10.1	13.3
11025	2.4	3.2	4.2
11024	9.3	13.2	17.8
11023	2.0	2.8	3.6
11022	4.7	6.6	9.0
11021	1.8	2.4	3.2
11020	8.8	12.2	16.3
11019	2.7	3.7	5.0
11018	3.8	5.2	6.9
11017	3.8	5.1	6.8
11016	21.0	29.1	38.9
11015	2.5	3.5	4.6
11014	6.8	9.6	13.2
11013	5.8	8.0	10.9
11012	4.7	6.7	9.3
11011	2.5	3.4	4.4
11010	6.7	9.5	12.8
11009	3.4	4.6	6.1
11008	3.3	4.8	6.6
11007	3.1	4.4	5.9
11006	1.2	1.6	2.1
11005	1.9	2.4	2.9
11004	2.1	2.9	3.8
11003	3.4	4.6	6.0
11002	11.6	15.8	20.9
11001	3.4	4.5	5.9

Table 66

CRUSTAL ENRICHMENT FACTORS FOR PARTICULATE MOLYBDENUM RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102		<	
11101		<	
11100	0.00	1.87	6.17
11099	0.00	1.77	5.82
11098		<	
11097		<	
11096		<	
11095		<	
11094	0.00	2.04	6.75
11093		<	
11092	0.00	0.67	2.18
11091	3.50	7.47	12.19
11090		<	
11089	0.95	4.79	9.44
11088	0.00	3.33	10.88
11087		<	
11086		<	
11085		<	
11084		<	
11083		<	
11082		<	
11081	0.00	10.00	31.83
11080		<	
11079		<	
11078		<	
11077		<	
11076		<	
11075		<	
11074		<	
11073		<	
11072		<	
11071		<	
11070		<	
11069		<	
11068		<	
11067		<	
11066		<	
11065		<	
11064		<	
11063		<	
11062	0.00	0.85	2.85
11061		<	
11060		<	
11059		<	
11058		<	
11057		<	
11056		<	
11055		<	
11054		<	
11053		<	
11052		<	

Table 66 continued

CRUSTAL ENRICHMENT FACTORS FOR PARTICULATE MOLYBDENUM RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051		<	
11050		<	
11049		<	
11048		<	
11047		<	
11046		<	
11045		<	
11044		<	
11043		<	
11042		<	
11041		<	
11040		<	
11039		<	
11038		<	
11037		<	
11036		<	
11035		<	
11034		<	
11033		<	
11032		<	
11031		<	
11030		<	
11029		<	
11028		<	
11027		<	
11026		<	
11025		<	
11024	3.77	207.41	457.12
11023		<	
11022		<	
11021		<	
11020		<	
11019		<	
11018		<	
11017	1.15	3.65	6.73
11016		<	
11015		<	
11014		<	
11013		<	
11012		<	
11011		<	
11010		<	
11009		<	
11008		<	
11007		<	
11006		<	
11005	0.00	3.11	10.33
11004		<	
11003		<	
11002		<	
11001		<	

Table 67

CRUSTAL ENRICHMENT FACTORS FOR PARTICULATE NICKEL RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102	0.85	1.31	1.73
11101	0.93	1.40	1.87
11100	1.28	2.06	2.75
11099	1.58	2.35	3.03
11098	1.24	1.96	2.72
11097	1.48	2.09	2.70
11096	0.91	1.32	1.73
11095	0.91	1.49	2.10
11094	1.59	2.19	2.83
11093	2.07	2.86	3.72
11092	0.88	1.36	1.75
11091	0.73	1.17	1.58
11090	0.90	1.57	2.11
11089	0.97	1.63	2.17
11088	0.87	1.69	2.27
11087	0.92	1.51	2.04
11086	1.08	3.64	4.86
11085	0.00	2.11	2.76
11084	1.03	3.23	4.39
11083	1.14	3.09	4.10
11082	1.78	5.71	7.95
11081	0.67	2.21	2.84
11080	2.42	6.88	8.99
11079	0.97	5.16	7.02
11078	0.69	1.66	2.24
11077	0.71	1.66	2.21
11076	0.36	2.48	3.42
11075	0.42	2.19	2.94
11074	2.55	7.51	10.25
11073	0.00	2.24	2.98
11072	1.51	3.49	4.89
11071	1.55	2.89	3.74
11070	2.38	6.74	8.79
11069	0.06	1.88	2.64
11068	1.14	3.09	4.10
11067	0.75	1.61	2.15
11066	4.59	11.55	15.61
11065	0.52	2.23	2.94
11064	0.44	1.47	1.94
11063	0.73	1.38	1.82
11062	0.35	0.60	0.81
11061	1.78	2.72	3.54
11060	1.32	9.34	13.08
11059	1.56	8.22	11.14
11058	1.97	8.57	11.47
11057	1.16	2.98	3.91
11056	1.65	5.23	7.21
11055	0.96	2.30	3.08
11054	0.45	1.19	1.64
11053	0.62	1.21	1.62
11052	0.59	1.58	2.16

Table 67 continued

CRUSTAL ENRICHMENT FACTORS FOR PARTICULATE NICKEL RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051	0.85	1.93	2.52
11050	0.74	1.51	2.01
11049	0.67	1.43	1.92
11048	1.07	2.30	3.00
11047	0.89	1.59	2.17
11046	5.06	14.11	19.29
11045	1.19	1.90	2.51
11044	1.69	3.23	4.28
11043	1.07	1.83	2.45
11042	2.50	11.14	15.37
11041	0.97	2.32	3.15
11040	7.61	20.63	28.50
11039	0.96	1.69	2.32
11038	2.97	8.40	10.96
11037	0.72	1.81	2.33
11036	5.18	17.68	23.81
11035	0.17	1.78	2.43
11034	0.00	11.74	17.07
11033	0.00	0.88	1.18
11032	0.75	10.73	15.70
11031	0.00	1.93	2.60
11030	0.06	1.88	2.64
11029	0.49	1.02	1.39
11028	0.00	1.14	1.63
11027	0.75	1.61	2.20
11026	0.31	2.15	2.93
11025	0.03	0.92	1.29
11024	0.00	0.69	1.27
11023	0.13	0.96	1.44
11022	0.10	1.55	2.35
11021	0.72	1.43	2.02
11020	0.52	3.09	4.61
11019	1.12	2.03	2.75
11018	0.02	0.47	0.73
11017	0.63	1.24	1.67
11016	0.00	6.88	10.77
11015	0.05	0.96	1.51
11014	0.00	2.41	3.83
11013	1.70	3.73	5.22
11012	0.30	1.64	2.30
11011	1.71	2.94	4.11
11010	0.00	2.24	3.39
11009	0.20	1.55	2.34
11008	0.00	0.87	1.20
11007	0.11	1.19	1.67
11006	0.64	1.05	1.41
11005	0.10	0.22	0.32
11004	0.69	1.46	2.11
11003	0.82	1.90	2.74
11002	0.34	2.36	3.24
11001	0.78	1.75	2.39

Table 68

CRUSTAL ENRICHMENT FACTORS FOR PARTICULATE LEAD RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102	2.33	3.23	4.11
11101	2.79	4.10	5.48
11100	5.54	9.08	12.78
11099	4.77	8.04	11.43
11098	4.58	6.66	9.02
11097	5.52	7.85	10.39
11096	5.70	7.90	10.34
11095	9.61	13.25	17.43
11094	4.30	5.94	7.74
11093	8.09	10.92	14.11
11092	5.88	9.51	13.29
11091	5.45	8.27	11.22
11090	2.42	4.03	5.55
11089	2.33	3.92	5.40
11088	2.75	4.65	6.29
11087	2.86	4.40	5.93
11086	0.00	3.20	4.74
11085	0.00	2.82	4.35
11084	1.00	3.55	4.73
11083	3.99	8.03	10.90
11082	7.12	15.36	21.76
11081	2.28	5.19	6.94
11080	0.00	4.58	7.08
11079	0.00	3.56	5.87
11078	0.53	2.02	3.00
11077	0.81	2.27	3.24
11076	2.60	7.71	11.51
11075	0.88	4.16	6.14
11074	0.00	2.64	4.83
11073	0.45	4.60	6.54
11072	0.20	2.05	3.00
11071	1.69	3.95	5.58
11070	0.00	1.80	3.94
11069	0.28	2.76	3.86
11068	0.00	2.09	3.00
11067	2.67	4.60	6.16
11066		<	
11065	4.13	8.35	11.38
11064	1.24	3.67	5.45
11063	1.83	3.28	4.51
11062	1.13	1.87	2.61
11061	4.14	7.26	10.37
11060	2.71	13.70	19.18
11059	4.88	14.18	18.67
11058	0.97	9.77	13.75
11057	6.37	11.02	14.58
11056	3.22	8.95	12.68
11055	1.54	4.19	6.18
11054	3.82	6.22	8.44
11053	2.50	3.92	5.19
11052	7.29	11.47	15.55

Table 68 continued

CRUSTAL ENRICHMENT FACTORS FOR PARTICULATE LEAD RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051	6.08	9.45	12.31
11050	2.87	4.88	6.64
11049	2.38	4.08	5.51
11048	3.10	6.12	8.55
11047	2.55	4.27	5.91
11046	7.62	25.47	38.84
11045	2.44	3.90	5.28
11044	6.04	10.08	13.64
11043	3.19	5.08	6.87
11042	4.48	16.34	22.54
11041	3.27	5.78	7.67
11040	24.64	48.40	66.01
11039	2.84	4.42	5.95
11038	0.00	1.12	3.67
11037	4.40	8.19	11.45
11036		<	
11035	0.00	2.09	3.00
11034		<	
11033	0.00	1.30	2.08
11032		<	
11031		<	
11030	2.01	5.52	7.73
11029	3.14	5.00	6.75
11028	0.66	4.78	7.41
11027	1.96	3.83	5.44
11026	6.28	11.05	14.61
11025	1.83	4.05	5.66
11024	0.32	6.05	9.67
11023	0.68	1.87	2.62
11022	1.80	4.27	6.01
11021	0.52	1.08	1.45
11020	2.85	6.60	9.02
11019	1.31	2.46	3.36
11018	4.37	6.53	8.63
11017	1.43	2.60	3.59
11016	2.00	14.40	22.12
11015	0.00	0.45	0.82
11014	1.60	6.05	9.01
11013	0.18	1.87	2.70
11012	3.16	5.96	8.05
11011	0.99	1.84	2.54
11010	5.69	11.34	15.26
11009	1.68	3.67	4.99
11008	2.53	5.81	7.85
11007	2.17	4.89	6.95
11006	0.71	1.20	1.62
11005	5.99	7.36	8.93
11004	0.85	1.64	2.25
11003	1.23	2.51	3.49
11002		<	
11001	3.85	6.18	8.17

Table 69

CRUSTAL ENRICHMENT FACTORS FOR PARTICULATE TIN RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102		<	
11101		<	
11100		<	
11099		<	
11098		<	
11097		<	
11096		<	
11095		<	
11094		<	
11093		<	
11092		<	
11091		<	
11090		<	
11089		<	
11088		<	
11087		<	
11086		<	
11085		<	
11084		<	
11083		<	
11082		<	
11081		<	
11080		<	
11079		<	
11078		<	
11077		<	
11076		<	
11075		<	
11074		<	
11073		<	
11072		<	
11071		<	
11070		<	
11069		<	
11068		<	
11067		<	
11066		<	
11065		<	
11064		<	
11063		<	
11062		<	
11061		<	
11060		<	
11059		<	
11058		<	
11057		<	
11056		<	
11055		<	
11054		<	
11053		<	
11052		<	

Table 69 continued

CRUSTAL ENRICHMENT FACTORS FOR PARTICULATE TIN RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051		<	
11050		<	
11049		<	
11048		<	
11047		<	
11046		<	
11045		<	
11044		<	
11043		<	
11042		<	
11041		<	
11040		<	
11039		<	
11038		<	
11037		<	
11036		<	
11035		<	
11034		<	
11033		<	
11032		<	
11031		<	
11030		<	
11029		<	
11028		<	
11027		<	
11026		<	
11025		<	
11024		<	
11023		<	
11022		<	
11021		<	
11020		<	
11019		<	
11018		<	
11017		<	
11016		<	
11015		<	
11014		<	
11013		<	
11012		<	
11011		<	
11010		<	
11009		<	
11008		<	
11007		<	
11006		<	
11005		<	
11004		<	
11003		<	
11002		<	
11001		<	

Table 70

CRUSTAL ENRICHMENT FACTORS FOR PARTICULATE THORIUM RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102	0.89	1.08	1.29
11101	0.88	1.09	1.34
11100	0.99	1.21	1.48
11099	0.99	1.22	1.49
11098	1.01	1.23	1.51
11097	1.00	1.24	1.54
11096	0.94	1.18	1.48
11095	0.98	1.20	1.47
11094	1.01	1.25	1.55
11093	1.02	1.27	1.58
11092	1.00	1.21	1.47
11091	0.78	0.96	1.17
11090	0.76	0.92	1.11
11089	0.78	0.94	1.13
11088	0.79	0.95	1.15
11087	0.80	0.97	1.19
11086	0.68	0.90	1.17
11085	0.72	0.95	1.22
11084	0.77	0.94	1.15
11083	0.73	0.87	1.04
11082	0.81	1.01	1.26
11081	0.81	0.95	1.12
11080	0.75	0.93	1.14
11079	0.74	0.91	1.12
11078	0.87	1.06	1.29
11077	0.89	1.07	1.29
11076	0.83	1.01	1.23
11075	0.83	0.99	1.18
11074	0.83	1.00	1.21
11073	0.80	0.97	1.18
11072	0.88	1.07	1.31
11071	0.92	1.11	1.33
11070	0.77	0.97	1.21
11069	0.77	0.94	1.15
11068	0.78	1.03	1.32
11067	0.82	1.00	1.21
11066	0.31	0.68	1.13
11065	0.52	0.76	1.05
11064	0.78	0.97	1.20
11063	0.88	1.07	1.31
11062	0.83	1.00	1.22
11061	0.86	1.04	1.26
11060	0.80	1.03	1.32
11059	0.90	1.21	1.59
11058	0.54	0.82	1.16
11057	0.89	1.05	1.22
11056	0.66	0.84	1.07
11055	0.74	0.95	1.19
11054	0.80	1.00	1.25
11053	0.87	1.06	1.29
11052	0.78	0.96	1.19

Table 70 continued

CRUSTAL ENRICHMENT FACTORS FOR PARTICULATE THORIUM RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051	0.88	1.06	1.27
11050	0.90	1.08	1.30
11049	0.90	1.11	1.37
11048	0.90	1.10	1.33
11047	0.90	1.10	1.35
11046	0.77	0.98	1.24
11045	0.94	1.13	1.37
11044	0.94	1.13	1.36
11043	0.94	1.15	1.40
11042	0.67	0.99	1.41
11041	0.91	1.10	1.33
11040	0.76	0.93	1.14
11039	0.88	1.08	1.33
11038	0.65	0.96	1.33
11037	0.82	1.02	1.27
11036		<	
11035	0.82	1.08	1.37
11034	0.66	0.97	1.31
11033	0.94	1.09	1.27
11032	0.80	1.12	1.49
11031	0.65	0.88	1.17
11030	0.82	1.00	1.21
11029	0.86	1.04	1.26
11028	0.73	0.94	1.19
11027	0.83	1.02	1.27
11026	0.92	1.11	1.33
11025	0.85	1.03	1.24
11024	0.67	0.92	1.23
11023	0.86	1.05	1.27
11022	0.67	0.90	1.18
11021	0.90	1.08	1.30
11020	0.69	0.98	1.33
11019	0.81	0.99	1.22
11018	0.79	0.97	1.18
11017	0.84	1.03	1.27
11016		<	
11015	0.90	1.11	1.36
11014	0.90	1.27	1.74
11013	0.81	1.05	1.35
11012	0.82	1.07	1.40
11011	0.84	1.02	1.24
11010	0.91	1.17	1.49
11009	0.86	1.06	1.30
11008	0.85	1.02	1.21
11007	0.77	0.98	1.23
11006	0.69	0.84	1.02
11005	0.77	0.93	1.14
11004	0.74	0.90	1.10
11003	0.83	1.00	1.20
11002	0.78	1.09	1.47
11001	0.85	1.03	1.25

Table 71

CRUSTAL ENRICHMENT FACTORS FOR PARTICULATE URANIUM RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102	0.71	0.83	0.98
11101	0.70	0.86	1.05
11100	0.94	1.15	1.40
11099	0.90	1.09	1.32
11098	0.86	1.08	1.36
11097	0.81	1.01	1.24
11096	0.82	1.01	1.24
11095	1.08	1.34	1.66
11094	0.89	1.08	1.33
11093	1.13	1.39	1.70
11092	0.98	1.18	1.43
11091	0.87	1.05	1.26
11090	0.66	0.89	1.16
11089	0.70	0.88	1.09
11088	0.48	0.71	0.99
11087	0.74	0.94	1.18
11086	0.75	1.20	1.75
11085	1.46	2.04	2.74
11084	0.69	0.96	1.27
11083	0.72	0.89	1.10
11082		<	
11081	0.95	1.19	1.46
11080	0.75	1.37	2.14
11079	1.01	1.49	2.07
11078	0.79	0.98	1.21
11077	0.71	0.93	1.19
11076	1.01	1.42	1.92
11075	0.00	1.83	5.55
11074	0.83	1.51	2.35
11073	2.70	3.36	4.18
11072	0.76	1.08	1.50
11071	0.88	1.13	1.42
11070	0.95	1.58	2.36
11069	0.00	1.41	3.78
11068	0.44	1.08	1.82
11067	0.91	1.22	1.58
11066	0.50	1.60	2.95
11065	1.16	1.47	1.84
11064	0.56	0.74	0.96
11063	0.65	0.85	1.10
11062	0.73	0.91	1.14
11061	0.70	0.90	1.13
11060	0.90	1.74	2.78
11059	0.99	2.19	3.62
11058	1.09	2.03	3.16
11057	0.87	1.21	1.61
11056	0.85	1.27	1.77
11055	0.94	1.44	2.04
11054	0.77	0.97	1.22
11053	0.71	0.92	1.16
11052	0.82	1.06	1.35

Table 71 continued

CRUSTAL ENRICHMENT FACTORS FOR PARTICULATE URANIUM RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051	0.85	1.08	1.36
11050		<	
11049		<	
11048	0.79	1.95	3.35
11047	0.80	1.06	1.37
11046		<	
11045		<	
11044		<	
11043	0.82	1.02	1.27
11042	0.74	2.40	4.50
11041		<	
11040	0.85	2.67	4.83
11039	0.01	0.52	1.15
11038		<	
11037	0.63	1.27	2.04
11036	1.78	4.00	6.77
11035		<	
11034	7.80	11.03	14.73
11033	0.81	1.14	1.53
11032	3.81	5.71	7.95
11031	1.28	1.94	2.75
11030	0.65	1.04	1.51
11029		<	
11028	1.15	1.68	2.34
11027	0.71	1.01	1.39
11026		<	
11025	0.56	0.94	1.39
11024	0.87	1.30	1.84
11023	0.60	0.76	0.96
11022	0.95	1.29	1.72
11021		<	
11020	0.85	1.64	2.58
11019	0.57	0.79	1.06
11018	0.62	0.86	1.16
11017	0.60	0.80	1.04
11016		<	
11015		<	
11014	0.61	1.11	1.74
11013	0.53	0.82	1.19
11012	0.67	1.00	1.42
11011		<	
11010	0.73	1.32	2.04
11009	0.44	0.67	0.94
11008	0.30	0.64	1.03
11007	0.56	0.82	1.14
11006		<	
11005	0.52	0.67	0.85
11004	0.50	0.67	0.87
11003	0.71	0.96	1.27
11002	0.88	1.33	1.88
11001	1.40	1.86	2.40

Table 72

CRUSTAL ENRICHMENT FACTORS FOR PARTICULATE ZINC RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11102	2.02	3.16	3.98
11101	1.94	3.08	3.98
11100	1.76	4.36	5.89
11099	2.35	4.87	6.38
11098	3.30	5.51	7.41
11097	3.47	5.42	7.04
11096	2.96	4.58	6.00
11095	2.96	4.71	6.28
11094	4.56	6.40	8.11
11093	4.14	5.87	7.45
11092	4.71	7.99	10.52
11091	4.27	6.32	8.05
11090	1.26	4.36	6.25
11089	2.27	5.42	7.39
11088	1.72	6.36	8.87
11087	2.02	4.73	6.62
11086	0.00	2.06	10.08
11085	0.00	4.64	13.29
11084	0.00	5.38	12.60
11083	0.00	3.95	9.77
11082	0.00	7.36	23.22
11081	0.00	5.92	11.27
11080	0.00	16.73	32.37
11079	0.00	11.21	25.75
11078	0.00	3.67	7.74
11077	0.00	3.00	5.90
11076	0.00	6.77	14.07
11075	0.00	5.06	11.09
11074	0.00	11.78	26.23
11073	0.00	1.18	10.12
11072	0.00	4.29	9.46
11071	0.00	4.01	7.74
11070	0.00	4.62	18.62
11069	0.00	2.13	9.92
11068	0.00	4.85	10.55
11067	0.00	3.48	5.83
11066	0.00	6.53	31.76
11065		<	
11064	0.00	3.83	11.54
11063		<	
11062	0.30	1.83	2.88
11061	0.00	1.66	3.49
11060	0.00	15.41	43.46
11059	0.00	4.37	25.21
11058	0.00	9.33	31.08
11057	0.00	2.75	7.86
11056	0.00	5.92	16.86
11055	0.00	2.33	6.36
11054	0.00	1.63	4.85
11053	0.00	1.82	3.31
11052		<	

Table 72 continued

CRUSTAL ENRICHMENT FACTORS FOR PARTICULATE ZINC RELATIVE TO SCANDIUM (WEDEPOHL)

THE RANGE REPRESENTS AT LEAST
THE 90% CONFIDENCE LIMITS

SAMPLE NUMBER	MINIMUM	BEST VALUE	MAXIMUM
11051	0.00	2.04	5.22
11050	0.00	2.07	4.32
11049	0.00	1.90	4.12
11048	0.00	0.81	4.51
11047	0.00	1.87	3.99
11046	0.00	4.50	37.34
11045	0.00	2.99	5.21
11044	0.00	3.99	8.04
11043	0.00	2.03	4.31
11042	0.00	1.87	28.98
11041	0.00	1.27	4.70
11040	0.00	9.85	37.42
11039	0.00	2.56	4.20
11038	0.00	8.35	28.58
11037	0.00	2.79	6.77
11036		<	
11035	0.00	0.00	5.02
11034	0.00	79.66	137.72
11033	0.00	2.42	8.03
11032	0.00	10.48	51.08
11031		<	
11030	0.00	3.25	9.62
11029	0.00	2.55	4.44
11028	0.00	3.56	12.27
11027	0.00	2.60	6.62
11026	0.00	4.16	10.83
11025	0.00	1.94	6.46
11024	0.00	8.47	24.86
11023		<	
11022		<	
11021	0.00	2.46	4.40
11020	0.00	4.14	13.93
11019	0.00	3.14	6.20
11018	0.00	2.03	4.31
11017	0.00	2.01	4.06
11016		<	
11015	0.00	4.55	8.43
11014		<	
11013	0.00	3.36	8.50
11012	0.00	2.11	7.45
11011	0.00	2.35	3.92
11010		<	
11009		<	
11008	0.00	3.36	6.86
11007	3.00	12.56	17.91
11006	1.66	3.92	5.64
11005	2.58	3.76	4.85
11004	1.01	5.06	7.86
11003	0.00	3.91	6.82
11002		<	
11001	0.00	3.01	5.53